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Volume 84, No. 1001 August 1959

THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

DEATH

WE record with regret the death of

Patrick Murphy.

NORTH OF ENGLAND SECTION

THE twenty-second Summer Meeting of the Section was held at the Prince of Wales Hotel, Scarborough, from Friday, June 5th, to Monday, June 8th, 1959.

The Chairman of the Section, Dr. J. R. Edisbury, presided over an Ordinary Meeting at 10.15 a.m. on Saturday, June 6th, at which K. Durham, B.Sc. (Unilever Ltd.), lectured on "Ice Cream," illustrating the methods of production and physical and chemical examination by slides and samples.

On the Saturday evening, the party saw the comedy "Friends and Neighbours" at the Arcadia Theatre, Scarborough, and on the Sunday afternoon made a coach tour of Forge Valley and Silpho Moors, taking tea at Ravenscar.

SCOTTISH SECTION

A JOINT Meeting of the Section with the Polarographic Society was held on Friday, June 26th, 1959, in the Lecture Theatre of the Department of Chemistry, Queen's University, Belfast. The Chair for the morning session was taken by Professor C. L. Wilson, D.Sc., Ph.D., F.R.I.C., and for the evening session by Mr. A. F. Williams, B.Sc., F.R.I.C., Vice-Chairman of the Section.

The following papers were presented and discussed: "The Polarographic Investigation of Some Copper Complexes in Non-aqueous Solution," by Z. P. Zagorski; "Aspects of the Polarographic Behaviour of Rhenium and Technetium," R. J. Magee, M.Sc., Ph.D., A.R.I.C.; "The Application of Polarography to Tissue Respiration," by I. S. Longmuir, M.B., B.Chir.; "Potentiometric Acid - Base Titrations in Acetone - Water Solutions of Nitrocellulose," by L. R. Leake and G. F. Reynolds, B.Sc., F.R.I.C.; "The Polarographic Determination of Nitroglycerine," by A. F. Williams, B.Sc., F.R.I.C.; "The Polarographic Behaviour of Metallic Ions in Molten Nitrates," by R. L. Faircloth, B.Sc. F.R.I.C.; "The Polarographic Estimation of Mercury Fulminate," by J. Hetman, A.R.I.C.

In the afternoon there was a tour of the Laboratories of the new Chemistry Building of the University.

WESTERN SECTION

THE Summer Meeting of the Section was held jointly with the Poole and District Technical Group on Friday and Saturday, June 5th and 6th, 1959, in Poole. The Chair was taken by the Chairman of the Poole and District Technical Group, Dr. G. D. Muir, F.R.I.C.

At 7.30 p.m. on Friday, June 5th, in the Lecture Room of the Poole Generating Station, G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C., lectured on "The Work of the Public Analyst."

MICROCHEMISTRY GROUP

THE twentieth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, June 17th, 1959, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Vice-Chairman of the Group, Mr. C. Whalley, B.Sc., F.R.I.C.

A discussion on "The Microdetermination of Physical Constants" was opened by Dr. M. Sobotka.

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BIOLOGICAL METHODS GROUP

THE Summer Meeting of the Group was held on Thursday, June 4th, 1959, when members visited the Laboratories of the Cooper Technical Bureau, Berkhamsted.

Following a description of the work carried out at Berkhamsted, tours were made of the Entomological and Chemical Laboratories and the Field Research Station.

The thanks of the visitors were expressed by Dr. J. I. M. Jones, F.R.I.C., Chairman of the Group.

Obituary

HENRY DRYERRE

HENRY DRYERRE, M.R.C.S., L.R.C.P. (London), Ph.D. (Edinburgh), F.R.S.E., late Emeritus Professor of Physiology at the Royal (Dick) Veterinary College, Edinburgh, died on February 5th last in his 78th year. When he entered hospital shortly before his death, the friends who knew him well had a premonition proved to be only too well founded that he had started on his last journey.

He was born in 1881 in Blairgowrie, a son of the late H. Dryerre, poet, musician and journalist, who although no schoolmaster was not averse to teaching a little Latin and Greek. Dryerre had only one son, who was a doctor in the R.A.F. when killed in a car accident in 1941; he is survived by his second wife.

That much hackneyed Scottish phrase "Lad o'pairts" could with truth be applied to Harry Dryerre. He started off in life as a pharmacist and was quite successful in that field. He was 34 years of age before he started to study medicine, so it is obvious to all what good use he made of the 31 years left before retiral from the Royal (Dick).

However, even before that he was to have his first attack of the heart trouble that was to remain a menace to him throughout his remaining years. In fact, on quite a number of occasions only his own intimate knowledge of how to deal with his affliction, coupled with the brilliant skill of his wife, brought him back from the brink and enabled the damaged mechanism to be geared into activity once more.

Dryerre was just as good with his hands as he was with his head. If he had been an engineer, an electrician or even a carpenter there is no doubt at all he would have been equally successful. He had his kitchen at Lasswade fitted up as a workshop, and many a highly skilled craftsman has stared with envy and admiration at the wonderful collection of tools that could be put to such excellent use in a way no tradesman could better.

He was one of the founder members of the Scottish Section of the Society and took an active part in all its work. He was a Vice-President of the Society in 1947–48.

He had a very keen interest in cinematography, and together with the late Professor Ritchie started the Edinburgh Scientific Film Society at the end of the war. The majority of our Scottish members will remember with pleasure the shows that were arranged by Dryerre to display many of the newest scientific films and regret that there can be no more. He had many films of his own, all of extreme interest, his own sound equipment and his own projection unit. On occasion he could produce wonderful entertainment for his guests.

He got a fine chance to show his puckish sense of humour when tape recorders were having their first run of success. He would have a number of guests for a meal and would skilfully lead the conversation round to some topic that was sure to bring forth strong controversy. Afterwards, to his great glee, he would play back all the heated arguments, much to the consternation of his guests, who had known nothing of the recorder hidden underneath the table.

His passing will long be regretted by his many friends.

A. ANDREW

Ferrous Metallurgical Analysis

A Review

By B. BAGSHAWE

(*The Brown-Firth Research Laboratories, Princess Street, Sheffield* 4)

In recent years classical methods of chemical analysis have been supplemented and to some extent replaced by instrumental methods based on physical and physico-chemical principles; one of the major results of this has been the simplification and speeding up of repetitive work in works control laboratories. There have, however, been other important effects influencing the nature, accuracy and scope of analytical work. For example, the detection and determination of trace elements has been improved enormously as a result of the developments that have taken place in photometric, spectrophotometric and polarographic methods of measurement.

The use of photometric methods in the steel industry was initiated by Vaughan,[1,2] and this was followed by the large-scale adoption of systematised group schemes for the rapid determination of five or six constituents in the solution from a single weighed sample of steel. In addition to their usefulness in group schemes for routine analytical work, photometric methods also have the important advantage that they can be used, with a minimum of modification, as standard referee procedures for individual elements. There has, in fact, been a noticeable trend in the development of specific photometric procedures for purposes requiring the highest accuracy, and it is noteworthy that since 1948 the British Standards Institution[3] has approved ten such procedures for the determination of nickel, chromium, cobalt, manganese, copper, tungsten, molybdenum, silicon (two) and titanium in iron and steel. Many of these standard methods, by virtue of their simplicity, are ideally suited for regular use as day-by-day routine procedures. Modern spectrophotometers permitting measurements to be made at pre-selected wavelengths have enlarged the field for further development. Interference from foreign coloured ions or from reagent background colour can be eliminated or much reduced. This often permits a major simplification in operational technique, eliminating or reducing the number of separations required. Moreover, two or more elements may be determined selectively in the same solution; for example, titanium and vanadium by the peroxide reaction, by making measurements in turn at the appropriate wavelength for each of the two coloured components.

There has been a complementary development in the use of selective reagents, most of which are organic chemicals having specific or particular applications in colour reactions for photometric methods of analysis, *e.g.*, 2:2′-diquinolyl, 1:1′-dianthrimide, Solochrome cyanine R, 2-nitroso-1-naphthol, nitroso-R salt and toluene-3:4-dithiol. Apart from the colour reagents, the main developments have been in the use of perchloric acid as a general-purpose reagent, EDTA for complexometric titrations, and reagents used in solvent-extraction procedures.

Perchloric acid is probably the most valuable all-round addition to the armoury of the ferrous analyst, particularly for the analysis of highly alloyed steels. It is an excellent decomposition agent for the carbides in high chromium, molybdenum and other high-alloy steels, it is a better dehydrating agent for silica than is hydrochloric or sulphuric acid, it is useful for oxidising tervalent chromium to the sexavalent condition, and when chromium is not wanted it can easily be removed as volatile chromyl chloride from fuming perchloric acid solution. EDTA has a relatively limited application in steel analysis and its extended use is really dependent on the development of a wider range of selective indicators. At present we are limited, for practical purposes, to murexide or Eriochrome black, but neither is really ideal for complexometric titrations.

Solvent-extraction procedures are being used to an increased extent for the removal of major amounts of iron and for the selective extraction of coloured complexes of various elements, as a means of eliminating interfering substances and of concentrating the complexes so that photometric measurements can be made with increased sensitivity. Clarke and Rooney* have studied and compared the behaviour of solvents such as di*iso*propyl ether, *iso*-butyl acetate, *iso*butyl methyl ketone, amyl acetate and mixtures of these for the extraction of iron. *iso*Butyl acetate is preferred to di*iso*propyl ether mainly because it is less volatile and

* Personal communication from W. E. Clarke and R. C. Rooney: British Cast Iron Research Association.

there is no heating effect with consequent pressure build-up on shaking. Amyl acetate is cheaper, but much of the original work was done in connection with the determination of trace elements, and *iso*butyl acetate is usually of higher purity in this respect. The extraction is useful as a preparatory treatment before the determination of traces of nickel, manganese, cobalt, aluminium, lead and some other elements. Sodium diethyldithiocarbamate can be used to remove iron, manganese, nickel, copper, cobalt and a number of other heavy metals, the complexes being extracted into chloroform. This has been used by Rooney[4] for the removal of interfering elements before extracting aluminium with cupferron into chloroform. Chromatography on cellulose and both anion- and cation-exchange resins are being used as column techniques for the differential elution of individual ions or groups of ions. This has important potential applications in the isolation and concentration of required constituents for colorimetric analysis, but the outstanding established development is in connection with the separation of niobium and tantalum,[5] which is otherwise extremely difficult and often unreliable.

Radioactivation techniques have been applied in one or two specialised directions; for example, Smales and his co-workers have determined traces of tantalum,[6] and cobalt, copper and nickel,[7] in steel by activation techniques. Such methods are potentially valuable for the determination of trace elements, but most works laboratories at present lack the facilities for carrying out activation analysis.

The polarograph has only a very limited application for the direct analysis of steel solutions, mainly because the reduction of tervalent iron produces a wave that tends to swamp the waves of other elements, but copper and lead can be determined most conveniently in the same solution as a direct routine procedure. Polarography may, however, be used as a sensitive method of measuring a variety of trace elements, for example, lead, aluminium, cobalt and tin, after preliminary separations to isolate the required element. Square-wave polarography[8] is a comparatively new development; it may result in a much extended scope for the application of direct methods without interference from the major constituents.

In the field of emission spectrography, the most important development in recent years has been the use of photomultipliers with associated electronic equipment for the direct reading of line intensities instead of the photographic process used with the conventional spectrograph. Direct-reading instruments are now in use in several of the large steelworks where the number of determinations and the speed at which it is necessary to obtain results justify the cost of the equipment.[9] Vacuum-emission and X-ray fluorescence equipment are further extending the field of application. Vacuum-emission spectrographs[10] in which the whole system from source to receiver is in effect evacuated or filled with an optically non-absorbing atmosphere permit the determination of the non-metallic elements carbon, sulphur and phosphorus. X-ray fluorescence[11] has decided potentialities for the determination of alloying elements in steels. There are, however, increasing limitations in applying it to elements having atomic numbers below that of titanium, *i.e.*, atomic number 22. Solution spectrography, which has the advantage of being independent of chemically analysed standards, has made some progress and has been used for the determination of minor amounts of niobium, tantalum, zirconium, aluminium or cerium after a preliminary chemical concentration procedure.[12]

Up to about thirty elements may be found in steel, either added intentionally as alloying constituents or present inherently as native impurities. Twenty-five of these are reviewed in the following discussion, and for convenience they are presented in alphabetical order.

Aluminium

There is no really good all-round method for determining aluminium in steel. The quantitative separation of small amounts of aluminium from large amounts of iron, chromium, nickel and other elements is a difficult operation and calls for a high degree of analytical skill. Because of the difficulties, recent investigational work has been directed towards the use of selective-extraction procedures and the application of sensitive colour reactions. This permits a more elegant treatment based on comparatively small sample weights, whereas with the older methods the required sensitivity can only be obtained by the expert manipulation of classical separation techniques applied to solutions of large weights of samples. The British Standard method,[13] although comparatively recent, suffers from these disadvantages. It depends on separation of iron, chromium, nickel and other interfering elements by mercury-cathode electrolysis[14] on a 10-g sample, precipitation of aluminium with 8-hydroxyquinoline,

after interfering residuals have been complexed with cyanide, and bromimetric titration of the organic radicle. The method is slow and cumbersome, but it has a wide range of application and is capable of giving excellent results when expertly used. It is, however, severely limited in accuracy below about 0·01 per cent. of aluminium, as 1 mg of aluminium (maximum sample weight 10 g) is the minimum that can be precipitated quantitatively with 8-hydroxyquinoline. The only way in which it is possible to improve this limiting sensitivity is by first extracting most of the iron with ether or amyl acetate from 20 to 50-g samples before applying the mercury-cathode electrolysis.

There are many other applications of classical procedures still in use. For example, separation of aluminium and chromium from most of the iron (ferrous) by bicarbonate hydrolysis followed by the oxine procedure[15]; mercury-cathode separation and then precipitation of aluminium with cupferron from formic acid solution, after first removing titanium and residual iron with cupferron from mineral acid solution[16]; precipitation as phosphate from ferrous solution with sodium thiosulphate.[17] All of these are laborious methods capable of good accuracy for certain steels and within certain limits, but having similar limitations to those of the British Standard method for accurate determination in trace ranges. The phosphate method in particular is severely limited in scope and is really only suitable for plain and low-alloy steels.

A rapid method sometimes used for high aluminium contents is the "soda" method, in which the solution of the steel is slowly added to an excess of sodium hydroxide and the resulting mixture is boiled to extract the aluminium as soluble aluminate. After the iron, chromium and other elements have been removed by fractional filtration, the aluminium is determined as phosphate or oxine. This method gives good results for steels containing 0·5 per cent. or more of aluminium, but it is not always appreciated that nickel modifies the chemistry of the sodium hydroxide extraction and results in loss of aluminium in the precipitated hydroxides. Molybdenum and vanadium, which are extracted as soluble molybdate and vanadate with the aluminate, also interfere, and further separation is necessary if these elements are present.

For the accurate determination of traces of aluminium, colour methods are used based on the reaction with aluminon (triammonium aurintricarboxylate) or with Solochrome cyanine R. Both methods are critically dependent on the strict observance of prescribed conditions, but Solochrome cyanine appears to have a definite advantage in this respect. Aluminon is more susceptible to minor changes of temperature, and a critical heating treatment, which must be very carefully controlled, is essential for reproducible colour development, whereas the Solochrome cyanine R colour can be developed at room temperature.

When the aluminon method is applied to steel, iron and chromium must be removed. Most of the iron can be extracted with di*iso*propyl ether and the remainder with an ether-saturated solution of cupferron. After removing the residual organic matter the aluminon colour is developed and determined spectrophotometrically at 545 mμ.[18]

Scholes and Smith[19] have recently developed a procedure for steel based on Solochrome cyanine R. The reaction is applied after a simple form of mercury-cathode separation and removal of remaining interfering elements with sodium hydroxide. The method has a precision of $\pm$0·001 per cent. in the range 0 to 0·035 per cent. of aluminium. Scholes and Smith have also applied the Solochrome cyanine R reaction after Bishop's[20] chromatographic separation of iron through a cellulose column with a solution of ethyl methyl ketone in hydrochloric acid. Aluminium is afterwards eluted from the column with dilute hydrochloric acid. Bishop[20] determined the aluminium in the eluate polarographically in a neutralised perchloric acid solution buffered with sodium acetate. There is interference from the nickel remaining on the column with the aluminium and which is subsequently eluted with it. Separation from other alloying elements is by no means complete and the direct method is, therefore, limited to plain and simple alloy steels.

Rooney[4] has described a method for the determination of traces of aluminium in cast iron in which iron and other interfering elements are removed by selective extraction into chloroform as diethyldithiocarbamate complexes. The aluminium is then extracted as cupferrate into chloroform at pH 4·5 and determined polarographically, the conditions specified by Willard and Dean[21] being used. For infra-trace amounts, *e.g.*, $<$ 0·004 per cent. of aluminium, larger samples must be used and most of the iron must be extracted with *iso*butyl acetate before the diethyldithiocarbamate complexes are extracted, or, if chromium or other alloying elements are present in quantity, mercury-cathode electrolysis can be applied to replace the

*iso*butyl acetate and diethyldithiocarbamate extractions. By using a cathode-ray polarograph and paying special attention to the blank values of reagents, Rooney has determined traces of aluminium as low as 0·00003 per cent. in both plain iron and iron containing 4 per cent. of chromium. The procedure is adaptable to steel.

Alumina, or other compound forms of aluminium, such as the nitride, is determined separately by methods based on insolubility in various solvent media in which elemental aluminium, iron and other metallic elements can be completely extracted. Dissolution in mineral acids, for example, 20 to 30 per cent. hydrochloric acid, is a somewhat arbitrary procedure, but is a quick and ready means of determining "acid-insoluble" alumina. Some alumina is attacked, depending on the form and size of the inclusions, the nature, concentration and temperature of the acid and the time of contact. Better results are obtained by using a less vigorous method of attack, for example, bromine - methyl acetate mixture, alcoholic iodine or alcoholic bromine. After the residue has been fused and residual interfering elements have been removed by mercury-cathode electrolysis, the aluminium in the electrolyte can be determined by the usual procedures, thus giving a measure of the aluminium in combination with oxygen and nitrogen.

A common error in determining alumina in residues from selective-solvent procedures is to assume that the alumina is readily decomposed by fusion salts, *e.g.*, potassium bisulphate or sodium carbonate. It should be borne in mind that the alumina in steel has been subjected to high temperatures and is often present in a very refractory form, for example, as corundum. To be certain of complete decomposition, the residue should be sintered at 1200° C with about twice its weight of an anhydrous mixture of 5 parts of sodium carbonate and 1 part of sodium tetraborate.

Arsenic

Methods for arsenic have been investigated in recent years. Evans's original method,[22,23] based on reduction and precipitation of elemental arsenic with hypophosphite and titration with iodine, has been improved, and a modified procedure has recently been issued as a British Standard.[24] The main features of the investigational work[25] from which this method was derived were the development of optimum conditions for the quantitative reduction to elemental arsenic with hypophosphite and the use of phosphoric acid to form non-reducible and hence non-interfering complexes of molybdenum, vanadium and tungsten. The method thus became universally applicable to all classes of iron and steel, and highly alloyed steels, including permanent-magnet alloys, and high chrome - nickel rustless and heat-resisting steels can now be analysed for arsenic with the same facility and accuracy as simple carbon and low-alloy steels. The hypophosphite method has largely replaced the older distillation procedure based on the volatility of arsenious chloride and iodimetric titration of the distillate. The distillation method is comparatively slow and is somewhat inconvenient for routine batch analysis owing to the need for a battery of distillation units.

Distillation is sometimes used preparatory to a photometric determination.[25] In this method the arsenic is distilled as halide from sulphuric acid solution after reduction with a mixed potassium bromide - hydrazine sulphate reagent. The determination is completed photometrically by converting the arsenic to arsenomolybdic acid and measuring the molybdenum blue produced with hydrazine sulphate. The colour intensity is critically dependent on the relative concentrations of acid, molybdate and hydrazine sulphate, and erratic results are obtained unless the optimum amounts of these reagents are strictly adhered to in both test and calibration solutions.

Boron

Traces of boron in steel (0·001 to 0·01 per cent.) have raised difficult analytical problems. The classical method based on distillation as methyl borate and alkalimetric titration is not applicable, as the traces normally present in steel are below the satisfactory titratable level, and the problem has arisen of finding the most suitable colour reagent. The choice is somewhat limited, but curcumin, quinalizarin, 1 : 1′-dianthrimide and carmine have all been used with various degrees of success. Separation of the boron from the main constituents of the steel is usually necessary, particularly with alloy steels, and this may be achieved by mercury-cathode electrolysis, distillation as methyl borate, sodium hydroxide, or by means of a cation-exchange resin.

Curcumin develops a sensitive red colour with boron on evaporation to dryness in the presence of oxalic and hydrochloric acids. The colour is extracted in alcohol and measured

spectrophotometrically at 550 mμ. The reaction conditions are extremely critical and require rigid standardisation; this has militated against its general adoption for steel analysis. It has, however, been applied successfully by Strickland and his co-workers[26] to various atomic-energy materials and by Chirnside, Cluley and Proffitt[27] to determining traces of boron in nickel.

Quinalizarin, 1:1′-dianthrimide and carmine all have the disadvantage that the reaction must be carried out in nearly concentrated sulphuric acid and some time is required for full colour development. 1:1′-Dianthrimide is about twice as sensitive as carmine, and, compared with these, quinalizarin is of relatively poor sensitivity. Quinalizarin is also of uncertain quality and different supplies give variable colour response. It has been used by Rudolf and Flickinger[28] as the basis of a rapid direct method for steel, in which the steel is dissolved under reflux in sulphuric acid, the ferrous sulphate is "salted out" from 95 per cent. sulphuric acid and the quinalizarin reaction is applied to the concentrated extract. The method gives fair results on plain and simple alloy steels, but it is not suitable for alloy steels forming coloured salt solutions, *e.g.*, chromium steels.

The B.I.S.R.A. Methods of Analysis Committee[29] has recommended the use of 1:1′-dianthrimide in a method for plain and low-alloy steels. Iron and other interfering elements are removed by cation exchange on Amberlite IR-120 and the blue dianthrimide complex is formed in the eluate and measured at 640 mμ. The reaction appears to be sensitive to the temperature and conditions of development. A 16-hour development period at 95° ± 1° C is specified, and attempts to accelerate the reaction by increasing the temperature usually result in brown discoloration arising from the action of sulphuric acid on the reagent. With plain and low-alloy steels the method is capable of a reproducibility to within ±0·0005 per cent. in the range below 0·005 per cent. of boron. It is less satisfactory for highly alloyed steels, particularly at higher boron levels, *e.g.*, 0·01 to 0·02 per cent. The main interfering elements are vanadium, which gives a brownish complex, and chromium, which may not be completely removed on the cation-exchange resin and gives background interference.

Carmine has not so far received much attention for steel analysis, but although it is rather less sensitive than 1:1′-dianthrimide it has the important advantage that the colour can be developed at room temperature. The reaction requires a minimum of 2 hours for full colour development, but it is preferable to allow an overnight standing period. The colour is photo-sensitive and must be protected from light during the standing period. This reagent may be applied after a cation-exchange separation, or alternatively the colour may be developed directly in the steel solution and measured spectrophotometrically at 610 mμ, provided that compensation is made for the absorption of chromium, nickel and other coloured ions.

Carbon

The conventional method for the determination of total carbon depends on high-temperature combustion in oxygen and gravimetric evaluation of the evolved carbon dioxide after absorption in a solid reagent, such as soda asbestos. This forms the basis of the recommended British Standard method.[30]

Although the gravimetric method is to be preferred, the determination may be completed volumetrically by absorption of the carbon dioxide in barium hydroxide and titration of the excess of alkali with standard acid or gas volumetrically in a Ströhlein-type apparatus. Both these alternatives are used extensively in works routine practice. The main disadvantage of the titrimetric method is that barium hydroxide solution is not an ideal absorbent for carbon dioxide, particularly at gas velocities exceeding 0·5 litre per minute, and it is also difficult to prepare and maintain the solution without contamination from atmospheric carbon dioxide. The Ströhlein gas-volumetric method is extremely rapid, *i.e.*, 2 to 3 minutes for a determination, but for accurate measurements in the gas burette it is necessary to limit the volume of oxygen required to a minimum; this demands a high temperature, *e.g.*, 1200° C, and the most severe fluxing conditions to ensure complete combustion.

The combustion method is applicable to all types of iron and steel, but inexperienced operators often obtain low results with high chromium - nickel stainless and heat-resisting steels. It is essential that the sample should be finely milled; coarse drillings or borings are inadmissible, a high combustion temperature is necessary (1150° to 1200° C) and a good flux must be used. Red lead, strip lead or tin is usually adequate, but with some heat-resisting steels an addition of pure extra-low-carbon iron may also be necessary to ensure complete combustion.

The combustion is normally carried out in an electrical-resistance furnace, but radio-frequency heating units are being used, particularly in America, where commercial units are available. This method has the advantage of a higher working temperature, extremely rapid combustion and localisation of the heat within the sample itself. Blanks are usually very low, as fluxes or accelerating agents are seldom necessary. The power consumption is much lower than for a resistance furnace and the unit is available immediately, without the lengthy heating-up period normally required. This, in particular, is a useful advantage for intermittent laboratory work where spasmodic determinations are required at short notice. The main disadvantages are the relatively high installation cost and a tendency for results to be a shade low. Low results appear to be due to cessation of the induction reaction and rapid loss of heat from the oxidised charge before fusion is complete. A small bead of unchanged metal remains enclosed in the core of the charge, and this may account for an error of up to 0·005 per cent. of carbon, irrespective of the carbon content of the sample. If this degree of error is not tolerable, complete fluxing can be obtained by restricting the sample weight to not more than 1 g, but the practical value of this is limited, for routine work, owing to the need for a more refined method of final measurement.

The precision of the conventional combustion method in its various forms is of the order of $\pm$0·01 per cent. of carbon over the usual working range. This is adequate for general purposes, but for very low carbon contents ($<$ 0·05 per cent.) there have been demands in recent years for more refined methods of determination. The simplest approach and one that has been used for batch routine work is to adapt the conventional method to operate on several multiples of the normal factor weight.[31] This requires an enlarged combustion tube and boats capable of carrying up to 16·362 g of sample (6 $\times$ 2·727 g) together with a semi-micro Midvale bulb for absorbing the carbon dioxide in soda asbestos. One operator using this method with a four-tube furnace can make up to 100 determinations in a day, and a reproducibility of within $\pm$0·002 per cent. can be obtained consistently in routine practice.

If higher accuracy is required, the low-pressure methods, all of which are variations of Yensen's original procedure,[32] can be operated to fourth-figure accuracy limits, *i.e.*, to within $\pm$0·0005 per cent. Recent adaptations of the procedure have been described by Wells[33] and Cook and Speight.[34] The method depends on conventional combustion and then evacuation of the combustion gases through a liquid-oxygen trap, in which the carbon dioxide is condensed and retained. The solid carbon dioxide is then vaporised into a known volume and its pressure is measured with a McLeod gauge. A method of similar accuracy has been described by Still, Dauncey and Chirnside[35]; it depends on the change of electrical conductivity occurring when the carbon dioxide is absorbed in barium or sodium hydroxide. A specially designed conductivity cell is used; it permits continuous circulation of the absorbing liquid and measurement of the conductivity at any time without stopping the oxygen flow. This method, like the low-pressure method, is capable of meeting the most stringent accuracy requirements in low-carbon ranges and it may also be used as a semi-micro method for steels of higher carbon content by suitably reducing the sample weight.

Free carbon or graphite is determined in pig and cast irons and also in certain types of graphitised steel. The choice of method is limited and the determination is often complicated by sampling problems arising from dusting losses of graphite during machining and subsequent segregation from the millings or drillings. It is now considered best practice to avoid drilling or milling altogether and to work on solid specimens of suitable weight and dimensions cut from particular locations in the pig or casting. This also applies to the determination of the total carbon content, and the difference between the two results is taken as the combined carbon.

The accepted method for graphite[36] depends on dissolution of the sample in nitric acid and separation of the graphitic residue on a carbon-free filter (porous alumina or silica grid with asbestos pad). The filter is washed and dried, and the graphite is burned *in situ* and determined by the conventional method for carbon. The accuracy of the method depends on immunity from acid attack on the graphite and complete dissolution of metallic carbides. The latter is not always realised, particularly with alloy irons containing acid-resistant carbides of chromium and molybdenum.

There are no entirely satisfactory methods for the direct determination of combined carbon and for this reason it is usual to obtain the combined carbon indirectly from the difference between the results of the total-carbon and free-carbon determinations. The Eggertz colorimetric method based on the brown colour of the solution of the nitrated carbon

compounds in nitric acid is sometimes used, but the colour is not directly proportional to the combined-carbon content and is modified by the nature of the carbides present and the metallurgical condition of the sample. It might have a limited application to samples of closely known type and history, but it is practically useless for general application to materials of different origin and composition.

Donaldson[37] proposed a direct method for combined carbon, in which the sample, contained in a closed system, is dissolved in a dilute nitric - sulphuric - phosphoric acid solution containing a small amount of silver nitrate as catalyst. The carbonaceous gases are passed over heated copper oxide and the carbon dioxide produced is absorbed and determined by the usual methods. The method requires a complicated all-glass apparatus, the manipulation is slow and laborious and the results are not very reproducible.

Carbon may also be determined by purely physical methods, for example, by means of a vacuum spectrograph[10] or by various methods based on the relationship between carbon content and magnetic properties.[38] The former is potentially similar in accuracy to the conventional chemical method. Magnetic methods are useful for furnace-stage control work, provided that they can be applied under rigidly standardised conditions, but their value as quantitative methods of measurement is really limited to plain carbon and simple alloy steels.

Chromium

The determination of chromium presents no major difficulties. The traditional volumetric methods all depend on quantitative oxidation to the sexavalent condition and measured reduction of the oxidation product. Oxidation from the tervalent to the sexavalent condition may be made with potassium permanganate, ammonium persulphate or perchloric acid. Oxidation with permanganate, the basis of the old Vignal method, is now less frequently practised. It is slower than the other two and has the disadvantage that considerable manganese dioxide is produced from the reaction between bivalent and septavalent manganese. This tends to give a positive error, if the manganese dioxide is removed by filtration, owing to colloidal manganese dioxide passing through the filter. Reduction of the manganese dioxide with hydrochloric acid may give low results owing to slight reduction of chromium, as a considerable amount of hydrochloric acid is usually necessary. Oxidation with ammonium persulphate is free from these disadvantages and the reaction is much quicker. In the presence of phosphoric acid and a silver catalyst, no manganese dioxide is formed, the manganese being oxidised directly to permanganate. This can be selectively reduced with hydrochloric acid, sodium nitrite or oxalic acid; hydrochloric acid is most commonly used. As in this case the permanganate is derived only from the manganese in the steel, a comparatively small amount of hydrochloric acid is necessary for its reduction, and there is, therefore, less risk of reducing the chromium. This is the principle adopted in the recommended British Standard method.[39] The same principle is also used in the British Standard for chromium in ferro-chromium alloy,[40] the main difference being in the method of titration. In the method for steel, the excess of ferrous sulphate is titrated with potassium permanganate, as this cancels out the simultaneous titration reaction of vanadium. In the method for ferro-chromium the back-titration is made with potassium dichromate, as vanadium is rarely present in ferro-chromium and advantage can, therefore, be taken of the superior end-point obtained with diphenylamine.

Oxidation with perchloric acid is extremely quick and has particular advantages for a rapid routine method. Heating to fumes with perchloric acid fulfils the three-fold purpose of expelling volatile acids used as initial solvents, decomposing stable residual carbides and oxidising tervalent chromium to the sexavalent condition in a single continuous operation. The chromic acid can then be determined by the usual titration method on an aqueous extract of the fumed concentrate. Interference from chlorine, which is developed as a secondary product of the oxidation reaction, is prevented by displacing it from the solution with carbon dioxide generated *in situ* by the addition of sodium carbonate. By this method determinations can be made in about 20 minutes. The results tend to be slightly low, probably owing to side reactions involving the formation of traces of hydrogen peroxide, or of hydrochloric acid, which may result in loss of chromium as chromyl chloride. Decomposition of resistant carbides is an important secondary function of perchloric acid oxidation, as it permits a uniform treatment for all steels. The other methods sometimes fail to decompose all the carbides, particularly with high carbon - chromium steels, and long digestion or other specialised treatment may be necessary.

Colorimetric methods are usually based on a measurement of the dichromate colour or of the colour produced by the reaction between dichromate and diphenylcarbazide. The former is used as a general method for up to about 3 per cent. of chromium, whereas the more sensitive diphenylcarbazide reaction is reserved for determination of traces or for minor residual amounts below about 0·3 per cent. For direct measurement as dichromate, methods based on oxidation with ammonium persulphate and silver nitrate,[1] potassium bromate,[41] perchloric acid[42,43] and mixed phosphoric - perchloric acid[44] have all been used in established practice. Ammonium persulphate is the least satisfactory of these reagents, as manganese is also oxidised to permanganate, which must be reduced selectively. There is also a risk of error from turbidity caused by traces of chloride precipitated by the silver catalyst. Oxidation with bromate is more satisfactory, as no permanganate is formed, but bromine liberated by the oxidation reaction affects the absorbancy and it is essential to remove it completely. When perchloric acid is used as the oxidant, dichromate colour complexes are formed with the ferric perchlorate; they are several times more sensitive than the equivalent of pure dichromate.[42] This principle has been investigated by the B.I.S.R.A. Methods of Analysis Committee.[43] The colour system was found to be critically dependent on the strict observance of prescribed conditions, it being affected by variations in acidity, temperature and iron concentration. The effect of iron is linear and if the amount present is known it can be allowed for in the calibration. With the exception of molybdenum and vanadium, none of the other elements normally present directly affects the colour reaction, other than by replacing its equivalent of iron, which, as just stated, can be allowed for. The method is useful as a quick routine procedure for small amounts of chromium ($< 0{\cdot}3$ per cent.), but it is not recommended for the most accurate work owing to the difficulty of controlling the above-mentioned variables. Oxidation with a mixture of phosphoric and perchloric acids produces a less sensitive colour, but the reaction is stabilised by the phosphoric acid and is much less critically affected by other variables.

The reaction with diphenylcarbazide is much more sensitive than any of the foregoing. Formerly, it was considered necessary to separate iron by precipitation with sodium bicarbonate or peroxide, but a direct photometric method, without separation, has been recommended by the B.I.S.R.A. Methods of Analysis Committee[45] and has been issued as a British Standard method.[46] Iron interferes strongly when the readings are made with a filter having maximum transmission at 5500 A, which is otherwise most suitable for the measurement of the chromium colour. The absorption due to iron is, however, much less with a filter having maximum transmission at 5700 A, which is still near to the peak of the absorption curve for chromium. In this way, disturbances due to variations in iron content are neutralised. The colour of the iron complex and also the corresponding colour produced by vanadium are also depressed by using a high phosphoric acid concentration. For the accurate determination of traces of chromium ($< 0{\cdot}03$ per cent.), larger samples must be taken and it becomes essential to remove iron. Any desired increase in sensitivity can be obtained by suitable choice of sample weight followed by solvent extraction of the iron with amyl acetate. For example, with 10-g samples, chromium can be determined with a precision of $\pm 0{\cdot}0002$ per cent. in the range 0 to 0·01 per cent.

Cobalt

The traditional method for the determination of cobalt in steel is based on precipitation with 1-nitroso-2-naphthol. Iron and chromium must be removed; this is usually done by zinc oxide or basic acetate separation. In both separations there is some adsorption loss of cobalt on the iron-group precipitate, up to about 1 per cent. of the amount present, and a further separation is necessary to recover this.

The cobalt complex with 1-nitroso-2-naphthol is of indefinite constitution and carries a good deal of free reagent; this necessitates its ignition to oxide. The oxide (Co_3O_4) is liable to be somewhat uncertain in composition ($XCoO.YCo_2O_3$) unless the ignition and cooling conditions are carefully controlled. The residue may be contaminated with traces of iron, chromium or copper and, particularly, with nickel if the steel is high in this element. In spite of its shortcomings the method is still used extensively, but it is time it was superseded by the more reliable photometric nitroso-R-salt method. It is, however, useful as a means of separating cobalt from large amounts of nickel and concentrating small amounts of cobalt preparatory to determination with nitroso-R salt.

The nitroso-R-salt method is simple, rapid and accurate and apart from some interference from large amounts of nickel and copper it is virtually specific for cobalt in steel. Both these elements interfere by consuming the available reagent, but the British Standard method[47] provides for up to 5 per cent. of nickel and 2 per cent. of copper without interference. The method can be extended to steels containing higher contents of nickel and copper by adding further calculated amounts of reagent, but it is probably better practice to separate the cobalt with 1-nitroso-2-naphthol.

For the accurate determination of trace amounts of cobalt (< 0·05 per cent.) the direct nitroso-R-salt method is not sufficiently sensitive and some means of concentrating the cobalt is necessary before applying the reaction. For pure iron the sample weight can be increased ten-fold or twenty-fold and the iron extracted with amyl acetate. For steels it is necessary to take account of nickel and copper, and various procedures have been recommended to meet the recent demand for determination of trace amounts of cobalt in steels required for atomic power plant applications. A method examined by the B.I.S.R.A. Methods of Analysis Committee[48] has given excellent results. This depends on separation of the iron group with zinc oxide, precipitation of cobalt with 1-nitroso-2-naphthol together with 5 mg of iron as carrier and photometric determination with nitroso-R salt. Loss of cobalt in the zinc oxide precipitate is below significance level, *e.g.*, about 0·0002 per cent. in the working range 0 to 0·04 per cent. The method is ideally suited to batch routine work and the results are reproducible to within ±0·002 per cent. for all classes of iron and steel and also for iron ore, ferro-alloys and nickel and chromium metal.

Methods of similar accuracy depending on the coloured complex formed by cobalt with 2-nitroso-1-naphthol have been recommended by Rooney[49] and Chirnside.[50] In Rooney's method, iron and copper are removed by extraction into chloroform with cupferron and after the residual cupferron has been destroyed the cobalt is extracted into benzene with 2-nitroso-1-naphthol and determined spectrophotometrically. In Chirnside's method, iron is complexed with sodium citrate and the cobalt complex with 2-nitroso-1-naphthol is extracted with chloroform and determined photometrically. Both are accurate and elegant procedures, but neither is quite so adaptable to large batch routine as is the previous method.

Other methods that may be used are photometric determination as thiocyanate after extraction with *iso*butyl methyl ketone[51] or as the tetraphenylarsonium cobaltothiocyanate complex after extraction with chloroform.[52,53,54] A radioactivation method has been successfully applied by Smales, Mapper and Wood.[7]

Volumetric methods are usually based on the potentiometric titration of the cobaltous ion with ferricyanide in ammoniacal citrate solution.[55] The reaction has been studied by Bagshawe and Hobson,[56] who found that the equilibrium constant for the reaction system is so low that the titration is always slightly incomplete at the point of inflexion and that the stoicheiometry of the corresponding manganese reaction, which occurs simultaneously, is affected to some extent by the concentration of other ions present in the solution. It is therefore difficult to make a precise correction for manganese. Nevertheless, the method has been found useful as a routine procedure for determining cobalt in comparatively high cobalt steels and a method has been recommended for permanent-magnet alloys[57] containing up to 30 per cent. of cobalt. These alloys are very low in manganese and the correction for this element is, therefore, of minor significance.

Copper

Copper is usually determined by iodimetric titration after separation with sodium thiocyanate, sodium thiosulphate or hydrogen sulphide, or photometrically with 2:2′-diquinolyl, sodium diethyldithiocarbamate or bis*cyclo*hexanone oxalyldihydrazone.

Precipitation with sodium thiosulphate or sodium thiocyanate is used in two British Standard methods for steel[58] and precipitation with hydrogen sulphide is used in a British Standard method for permanent-magnet alloys.[59] Precipitation with hydrogen sulphide is the most reliable for small amounts of copper, particularly if a carrier sulphide is also present, and for this reason it is preferred for the determination of minor traces of the element in pure iron after solvent extraction of most of the iron from a large weight of sample (10 to 20 g) with ether or amyl acetate. For normal copper contents in steel, precipitation with thiosulphate or thiocyanate is preferred. Thiocyanate is more specific than thiosulphate and may be used for a wider range of alloy steels, but the results tend to be about 0·01 per cent. low in the range below 0·1 per cent. of copper. Thiosulphate gives a better recovery in this range,

but tin, molybdenum and some vanadium are co-precipitated, and vanadium interferes with the iodimetric titration. Vanadium does not form a precipitate with thiocyanate and hence does not interfere. The thiocyanate precipitate is readily soluble in acids, preparatory to iodimetric titration, but the thiosulphate precipitate is associated with a lot of free sulphur and must be ignited before dissolution of the residue. Some authorities consider that molybdenum interferes with the iodimetric titration, and the American Society for Testing Materials[60] specifies a separation with sodium hydroxide for steels containing more than 0·25 per cent. of molybdenum. This is not a practice to be recommended, as copper is partially soluble in sodium hydroxide, depending on the excess of alkali, and in any case the treatment is unnecessary, as it has been shown[61] that the equivalent of up to 4 per cent. of molybdenum is without influence on the titration.

Determination with 2:2′-diquinolyl is the best of the colorimetric methods[62] and forms the basis of the recommended British Standard photometric method.[63] In this method iron and copper are reduced to the bivalent condition with hydroxylamine, the copper - diquinolyl complex is developed in ammoniacal citrate solution and extracted from the aqueous phase with *iso*amyl alcohol. A similar method has been proposed by Elwell,[64] who prefers sulphurous acid to hydroxylamine for reducing the copper, and he develops the copper - diquinolyl complex in a citrate - acetate buffered solution. Both methods give similar results for steels containing less than 1 per cent. of copper. Above this limit, neither is as accurate as the standard volumetric methods. For routine purposes the 2:2′-diquinolyl method can be simplified by reducing the copper with stannous chloride and developing the colour directly in a homogeneous aqueous medium, thus eliminating the extraction with *iso*amyl alcohol.

Determination with sodium diethyldithiocarbamate can be made directly in the steel solution[65] by using a colloid stabiliser, such as gum acacia in ammoniacal citrate solution, or after solvent extraction with butyl acetate,[66] chloroform[67] or carbon tetrachloride.[62] Each of these solvent extractions is made in the presence of EDTA as masking agent for interfering ions. In the direct methods, nickel and, particularly, cobalt and manganese often cause turbidity, and erratic results are caused by variations in the quality of gum acacia. Even with solvent extraction the interference of cobalt and manganese is not entirely eliminated, although it is much reduced.

Probably the simplest of the colorimetric methods is the one based on the blue colour developed with bis*cyclo*hexanone oxalyldihydrazone in ammoniacal citrate solution.[68] The method is applicable to a wide range of steels, and requires no separations or extractions; it can be completed in 20 to 30 minutes. It is, therefore, particularly suitable for repetition testing. The reproducibility is about $\pm 0{\cdot}015$ per cent. in the range up to 0·5 per cent. of copper. Large amounts of nickel or cobalt may cause some interference, but this can be minimised by more rigid control of pH and by increasing the alcohol concentration of the reagent solvent.

There is also an excellent polarographic method[69] by which copper and lead can be determined simultaneously in a base solution containing hydrazine hydrochloride and sodium formate. Ferrett and Milner[70] have utilised a square-wave polarograph to determine copper, together with lead and tin, in steel. The method can be applied directly to a solution of the steel in perchloric acid and the valency state of the iron is not so important as it is in the conventional polarographic method, for which it is essential that most of the iron must be in the ferrous condition.

Hydrogen

Hydrogen may be determined together with oxygen and nitrogen by vacuum fusion of a solid specimen of the steel in a carbon crucible, from which the resulting gases are pumped off and measured by the usual methods of gas analysis.[71] This is not a particularly accurate method, as hydrogen is slowly evolved from a cold steel sample, especially under a high vacuum, and the samples must be kept under these conditions during the 3 to 4 hours required for out-gassing the system.

Hydrogen can be quantitatively extracted from solid specimens without fusion and this is now the recognised procedure in works practice.[72,73] Vacuum heating for about 1 hour at 600° to 700° C gives complete extraction for ferritic steels, but high chromium - nickel stainless steels may require up to 3 hours at the same temperature. The total gas evolved is collected, measured volumetrically and reported as hydrogen although it may contain small amounts of other gases. The hydrogen content is usually over 90 per cent., and, as the total volume of

gas evolved is only of the order of 5 ml per 100 g of steel, there is no significant error in using this form of computation. If the true hydrogen content of the gas is required, it can be measured by differential diffusion through a palladium tube. Before determination, the sample is kept in solid carbon dioxide to prevent premature loss of hydrogen by normal atmospheric diffusion. The apparatus is designed so that the sample can be introduced into the vacuum system immediately before determination by means of a magnetic lift operating through a mercury seal, thus obviating the necessity for keeping the sample for long periods under vacuum.

A recent development[74] that offers potentially a major simplification of technique depends on the use of a streaming carrier gas instead of vacuum pumps to extract the gas evolved from the steel. The steel specimen (about 50 g) is heated in a silica combustion tube at 650° C through which nitrogen is passed at a rate of about 2 litres per hour. The hydrogen diffusing from the steel is carried in the stream of nitrogen, converted to water over a mixture of copper and ferric oxides at 550° to 600° C, absorbed in methanol and titrated with Karl Fischer reagent by a dead-stop end-point procedure.

Lead

Determination of lead is required in two distinct categories—(*a*) leaded steels of the "Ledloy" type containing 0·2 to 0·3 per cent. of lead, and (*b*) steels containing mere traces of lead ($<$ 0·01 per cent.) as an unwanted deleterious impurity. The requirements of the first group are met by the classical gravimetric procedures based on separation as sulphate or sulphide and subsequent conversion to molybdate. For the second category, sensitive colour reactions must be utilised. Polarographic methods can be adopted for determination in both categories.

The British Standard method[75] is based on separation as sulphate from a ferrous solution and precipitation as lead molybdate from an acetate solution of the sulphate, made alkaline with ammonia. The method gives reasonable results on "Ledloy" steels, but has several disadvantages. It is unreliable for lead contents below about 0·05 per cent., it is difficult to heat solutions of 10-g samples of steel to fumes with sulphuric acid under the specified conditions, the lead sulphate residue tends to be contaminated with iron and an ammoniacal acetate solution is not the best medium for the precipitation of lead molybdate. Precipitation as sulphide is to be preferred as a means of separation and a method examined recently by the B.I.S.R.A. Methods of Analysis Committee[76] is being put forward to supersede the British Standard method. This sulphide method has given results reproducible to within $\pm$0·01 per cent. in the range 0·07 to 0·26 per cent. of lead,[77] but it is not recommended for lead contents below 0·05 per cent. The sulphide precipitate is dissolved in hydrochloric acid and the lead is precipitated as molybdate from ammoniacal tartrate solution. Tartrate prevents co-precipitation of residual iron and for this reason is superior to ammoniacal acetate as the precipitation medium. Precipitation of lead molybdate from formic acid - formate solution would probably be superior to either, as when it is precipitated from acid solution it is more likely to be true to the theoretical formula than when precipitated from ammoniacal solution. Residual iron is not co-precipitated with lead molybdate from acid formate solution and the precipitate has better physical characteristics, it being denser and more crystalline than when precipitated from either acetate or ammoniacal tartrate solution.

For the determination of trace amounts of lead, only methods in which some form of selective extraction is used have much hope of success. The determination may be made by photometric measurement of the lead - dithizone complex after extraction with chloroform from an ammoniacal citrate - cyanide solution.[78] Iron in the amounts found in steel interferes and must be removed, for example, by extraction with amyl acetate. The method is satisfactory for carbon and low-alloy steels, but cannot be applied directly to chromium steels. Nickel also interferes, but the interference can be minimised considerably by increasing the cyanide content. Interference from chromium and nickel can be prevented by first "seeding" the lead as sulphide with a small amount of ferrous sulphide from a carefully neutralised perchloric acid solution. This principle has been successfully applied by Bricker and Proctor[79] in a dithizone procedure for lead in corrosion-resisting steels. Lead can be extracted as its diethyldithiocarbamate with chloroform at pH 11 from a cyanide - tartrate buffer solution and this has been utilised by Rooney[80] in a method for determining traces of lead and bismuth in cast iron. Iron is extracted first with *iso*butyl acetate and the determination is completed with a cathode-ray polarograph and an acidified tartrate base electrolyte.

This method has extreme sensitivity and traces as low as 0·0001 per cent. can be determined.

The direct polarographic procedure[69] applied in a sodium formate base solution with the iron in the ferrous condition is satisfactory for alloying amounts of lead. For "Ledloy" steels containing 0·2 to 0·3 per cent. of lead the accuracy is about equal to those of the conventional chemical procedures, but the polarographic procedure is much quicker and has the added advantage that copper can be determined simultaneously. Determination of lead together with copper and tin can also be made by square-wave polarography.[70] This can be applied directly to an oxidised solution of the steel and reduction of the iron to the ferrous condition is unnecessary.

Magnesium

Magnesium is determined in certain types of magnesium-treated cast iron, but only rarely in steel. The best method is that of Westwood and Presser,[81] which depends on solvent extraction of most of the iron with *iso*propyl ether, removal of manganese and certain other elements by electrolysis with a sodium-amalgam cathode and precipitation as ammonium magnesium phosphate after complexing residual interfering ions with citric acid.

La Rochelle and Fournier[82] used a similar method, but found that about 8 per cent. of the magnesium was lost when a conventional mercury-cathode electrolysis was used. The sodium-amalgam cathode subsequently introduced by Westwood and Presser eliminated this source of error, and quantitative recovery of the magnesium from the electrolyte can be obtained.

Magnesium can also be determined by titration with EDTA after removal of interfering elements. Large amounts of iron can be selectively extracted with ether, manganese oxidised to manganese dioxide and removed together with residual iron by means of a basic acetate separation. The magnesium in the filtrate can then be titrated with EDTA to the change point of Eriochrome black T. Green[83] recommends a zinc oxide separation of iron together with manganese as manganese dioxide and titration with EDTA after complexing zinc and other interfering ions with cyanide.

Colorimetric methods of determination by means of reagents such as Titan yellow or quinalizarin are not very satisfactory owing to the difficulty of completely removing all interfering elements.

Manganese

The most widely used methods for determining manganese are all based on titrimetric or colorimetric evaluation of permanganic acid. The best all-round method is the one based on oxidation with potassium periodate in sulphuric - phosphoric - nitric acid solution and photometric determination of the permanganic acid.[84,85] This method is universally applicable to all types of steel, simple to operate, rapid, remarkably free from interference and equally suitable for standard referee or works routine requirements. The permanganic acid produced by periodate oxidation is stabilised by the presence of the excess of reagent, which remains throughout; it is independent of silver catalysis, which is necessary if the oxidation is made with persulphate, and, under properly regulated conditions, the oxidation can be carried out selectively in the presence of tervalent chromium. Persulphate methods suffer by comparison, as persulphate decomposes rapidly in the boiling solution and the permanganic acid produced is therefore relatively less stable. Chromium is simultaneously oxidised to chromate and the solutions sometimes develop opalescence owing to traces of chloride precipitated by the silver catalyst.

Titrimetric methods are usually based on bismuthate or persulphate oxidation. Both methods are somewhat critical and tend to give low results, particularly with large concentrations of manganese, owing to partial decomposition of permanganic acid. The persulphate oxidation is carried out in boiling solution and requires a high concentration of phosphoric acid and silver nitrate for quantitative formation of permanganate in a fully stable condition. Chromium is also oxidised quantitatively to chromate. A high acidity prevents oxidation of cobalt, which tends to occur to some extent in dilute acid solutions. The permanganate can be titrated with sodium arsenite or with ferrous sulphate and potassium dichromate. Arsenite titration is popular in works routine practice, as it can be performed without interference in the presence of chromate equivalent to several per cent. of chromium. The arsenite titration reaction, however, is not strictly stoicheiometric and an empirical factor must be used to obtain precise results. Titration with excess of ferrous sulphate and back-titration with

potassium dichromate is superior for accurate work, but chromium is also titrated and must, therefore, be separated.

Bismuthate oxidation is carried out in cold solution and, as the chromium reaction is relatively slow at room temperature, the method can be operated without serious error in the presence of up to about 0·5 per cent. of chromium. Cobalt is oxidised in part and interferes to some extent. Permanganic acid formation is not completed immediately after adding the bismuthate and there is a definite risk of manganese dioxide being formed by the interaction of permanganate with unoxidised bivalent manganese. Manganese dioxide, once produced, is fairly stable in cold nitric acid solution and causes low results, as it is removed by filtration with the excess of bismuthate. The magnitude of the error is dependent on a variety of factors, but it is not likely to be serious unless the managanese concentration is very high. For this reason the bismuthate method is less satisfactory for ferro-manganese and ferro-silico-manganese than for steels of normal manganese content.

If chromium is present in interfering amount, a separation is necessary before applying either the persulphate or bismuthate methods. Zinc oxide is the one most frequently used and this is incorporated in the British Standard volumetric method.[86] There may be slight loss of manganese by adsorptive co-precipitation, but this is not usually sufficiently serious to warrant a repeat separation. Chromium can also be removed by volatilisation as chromyl chloride from fuming perchloric acid solution, but, although this is a convenient means of removing most of the chromium, it is not easy to ensure its complete removal. For this reason, zinc oxide separation is preferred.

Another method that is very useful, particularly for high-manganese steels and ferro-manganese alloy is that recommended by Lingane and Karplus,[87] based on the titration of bivalent manganese with permanganate in sodium pyrophosphate solution according to the reaction—

$$4Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} \rightarrow 5Mn(H_2P_2O_7)^{3-} + 4\,H_2O.$$

This is a strictly stoicheiometric reaction, but the titration must be carried out potentiometrically, as it cannot be made to a visually observable end-point owing to the pink colour of the pyrophosphate solution.

Molybdenum

The best method for molybdenum in steel is the one based on photometric measurement of the orange-red oxythiocyanate colour produced by the reaction between thiocyanate and quinquivalent molybdenum.[88,89] The reduction is made with stannous chloride, which also serves to reduce and decolorise the corresponding ferric thiocyanate formed simultaneously.

The coloured compound can be isolated and concentrated by extraction with organic solvents, such as butyl acetate or *cyclo*hexanol, but it is now more customary to develop the colour in homogeneous acid medium with perchloric acid as the stabilising agent. The bleaching of the ferric thiocyanate colour appears to be catalysed by molybdenum; it is rapid with high-molybdenum steels and comparatively slow, uncertain and sometimes incomplete with low-molybdenum steels. A high stannous chloride concentration is beneficial in reducing the coloured ferric compound, but a small amount of titanous salt, which acts as a reduction catalyst, is completely effective without increasing the stannous ion concentration.

There is interference from copper above about 0·4 per cent. owing to precipitation of cuprous thiocyanate, but the interference may occur at lower copper levels if a high stannous chloride concentration is used, as this reduces the solubility of cuprous thiocyanate. Vanadium and cobalt interfere only slightly, but a correction can be applied for the most accurate work. Tungsten can be held in solution as phosphotungstic acid or as a citrate complex; the latter is preferred. Most thiocyanate methods are critically dependent on a strict observance of prescribed conditions and this is no exception. Such factors as acidity and stannous chloride and thiocyanate concentrations are interdependent and must be carefully balanced to give optimum performance.

Molybdenum can also be determined very accurately by its colour reaction with toluene-3:4-dithiol. This principle is normally applied as a semi-micro method[90] for molybdenum alloy steels, but the iron concentration has no critical influence on the molybdenum reaction, and by increasing the size of the test aliquot it is possible to determine traces of molybdenum of the order of 0·01 per cent. or less to an accuracy of within $\pm$0·0002 per cent.

The classical gravimetric methods based on precipitation as sulphide, lead molybdate or with benzoin α-oxime are still used, but much less than formerly. The benzoin α-oxime

method is the best of these, but its scope is limited by the interference of residual amounts of tungsten. Because of this the method is complicated by the need for additional separations. The British Standard method[91] provides for a separation of residual tungsten (up to 0·5 per cent.) by wet oxidation of the mixed tungsto-molybdenum complex and separation of molybdenum as trisulphide from a buffered tartrate solution. The method can be used as a concentration procedure to separate traces of molybdenum from a large weight of sample preparatory to a determination by the thiocyanate colour method. By this means molybdenum below 0·05 per cent. can be determined with an accuracy to within ±0·001 per cent.

The lead molybdate method is usually applied after separating iron with sodium hydroxide, but is also used as a finishing method after a preliminary separation as sulphide or oxime. Tungsten and vanadium interfere in the direct procedure, but vanadium can be rendered non-interfering by boiling with formic acid, which reduces it and prevents its precipitation as lead vanadate. Formic acid solution is a better medium than acidified acetate solution for the precipitation of lead molybdate, as, apart from the control of vanadium interference that it permits, it also prevents contamination from aluminium and tin. The lead molybdate method gives good results on many steels, but above about 1 per cent. of molybdenum the results are usually about 3 per cent. high owing to the precipitation of basic molybdate containing an excess of lead oxide ($X PbMoO_4 . Y PbO$). This source of error can, however, be eliminated by re-precipitation.

Přibil and Malat[92,93] have described the use of EDTA as a complexing agent in the determination of molybdenum and tungsten with 8-hydroxyquinoline. Most of the cations normally precipitated with 8-hydroxyquinoline from acidified acetate buffered solution can be "fixed" as stable complexonates. By this means a fairly selective precipitation of oxines can be obtained, and from ammonium acetate - acetic acid solution only molybdenum, tungsten, vanadium and uranium are precipitated, most other elements being screened by the EDTA. A method has been proposed for ferro-molybdenum in which this principle is used, and little modification would be required to apply it to steel. The main limitation, however, is the interference of tungsten.

Volumetric methods, usually based on reduction with nascent hydrogen in a Jones-type reductor or with liquid amalgams, have been mainly limited to the determination of large amounts of molybdenum as, for example, in ferro-molybdenum. This type of method provides a convenient form of rapid assay, but it is unspecific and is subject to interference from vanadium, chromium, tungsten, titanium, niobium and several other elements.

Nickel

Nickel is usually determined volumetrically by titration with potassium cyanide and silver nitrate after precipitation with dimethylglyoxime.[94]

Considerable attention has been given in recent years to the interference of copper and cobalt.[95,96] Both elements tend to contaminate the glyoxime precipitate and interfere subsequently by reacting with cyanide. Copper interferes by consuming the available reagent and may thus cause low results. If more reagent is added, sufficient to precipitate all the nickel in the presence of the copper, the glyoxime precipitate is contaminated with copper and high results are obtained. It has been shown that co-precipitation of copper is a critical function of precipitation temperature. At low temperatures, *e.g.*, 20° C, contamination is at a maximum, but decreases progressively with rising temperature and at 90° C is barely significant. At this temperature up to 40 mg of nickel can be precipitated in the presence of 50 mg of copper without interference, and provided the precipitation is completed at 90° C no subsequent co-precipitation occurs on cooling before filtration.

Interference of cobalt is similar in some respects to that of copper, but it is more difficult to control. It is difficult to precipitate small amounts of nickel quantitatively in the presence of a high concentration of cobalt, and a large excess of reagent is not always effective. With larger amounts of nickel, extensive co-precipitation of cobalt occurs. The precipitates are much darker red than usual or may be brown, slimy and difficult to filter. Chirnside, Cluley and Proffitt[97] examined contaminated glyoxime precipitates by X-ray diffraction methods and reported the presence of a distinct second phase containing iron, cobalt and carbon. Weeldenburg[98] reported a compound containing one atom each of iron and cobalt and 3 molecules of dimethylglyoxime.

Various methods have been recommended to overcome cobalt interference. Oxidation to the cobaltic condition with hydrogen peroxide in the hot ammoniacal citrate solution

before precipitating with glyoxime is effective over a fairly wide range of cobalt concentrations. For example, up to 40 mg of nickel can be precipitated in the presence of 150 mg of cobalt.[95,96] The peroxide treatment must be applied in ammoniacal citrate solution; ammoniacal tartrate is much less satisfactory. Chirnside, Cluley and Proffitt[97] prevented cobalt interference by first reducing iron with sodium sulphite and precipitating the nickel glyoxime from acetate solution instead of from ammoniacal solution. Kirtchik[99] recommended a procedure in which nickel and cobalt are converted to non-ionised nickelo- and cobaltocyanides and the cobalt is selectively oxidised to the cobalticyanide with hydrogen peroxide. The comparatively unstable nickelocyanide is then decomposed with formaldehyde, and nickel glyoxime is precipitated without interference from cobalt. A modification of this principle has been recommended in the British Standard method[94] for the determination of small amounts of nickel in high-cobalt steels. Older methods, such as the separation of the cobalt with potassium cobaltinitrite or Evans's[100] cobalticyanide method are much less satisfactory than the three mentioned above.

Several alternative methods are available for completion of the determination after precipitation with dimethylglyoxime, but they are generally rather less satisfactory than the cyanimetric method. Titration with EDTA, with murexide as indicator, gives good results,[101] but the solution must be kept as free as possible from ammonium and other foreign salts that tend to impair the end-point. Oxidation of the glyoxime radicle with ferric sulphate and titration of the ferrous sulphate equivalent with permanganate or oxidation with an excess of potassium dichromate and back-titration with ammonium ferrous sulphate also give good results. Gravimetric methods based on direct weighing as glyoxime or as nickel oxide after ignition of the complex are seldom used in steel analysis. Although equally accurate, they are comparatively slow and generally less suited to repetition work.

Nickel can be determined without previous separation as glyoxime by direct cyanimetric titration in ammoniacal citrate or tartrate solution. A good light is necessary for the iodide end-point to be detected against the background colour of iron and other citrate complexes. Alternatively, iron may be precipitated with ammonia after converting the nickel to nickelocyanide and the excess of cyanide in a filtered aliquot titrated with silver nitrate. These are very old methods still used for rapid furnace-control purposes. Copper and cobalt interfere, but in their absence or if suitable correction is made for small residual amounts, surprisingly accurate results can be obtained.

Direct photometric methods are also used based on the colour of the oxidised nickel dimethylglyoxime compound. The oxidation may be made with bromine, iodine or iodate, and the colour is developed in ammoniacal solution containing the iron, chromium and other elements as soluble citrates. Determinations can be made in less than 30 minutes and the accuracy is to within $\pm 0{\cdot}01$ per cent. in the range 0 to 0·5 per cent. of nickel.[102] The method can be extended to higher nickel contents, up to 8 per cent. or more, but the conditions become increasingly critical with increasing nickel content and some loss of accuracy can be expected. Trace amounts of nickel ($< 0{\cdot}05$ per cent.) can be determined on large sample weights with dimethylglyoxime after solvent extraction of iron with ether or amyl acetate.

Niobium and tantalum

Determination of niobium and tantalum together presents no particular problem, but because of the difficulties attendant on the separation of the two elements, individual determination is not regularly attempted in works practice.

Separation of niobium and tantalum from the steel solution is usually accomplished by acid hydrolysis or by precipitation with cupferron. Precipitation by hydrolysis can be carried out in dilute hydrochloric, sulphuric or perchloric acid solution in a similar manner to the usual method for tungsten. Weiss and Landecker[103] stated that hydrolysis is complete from perchloric acid solution, and Silverman[104] used this principle in one of the earliest methods for steel. Cunningham,[105] however, showed that the presence of titanium prevented complete hydrolysis from perchloric acid solution, and Bagshawe and Elwell[106] obtained slightly low recoveries both from hydrochloric and sulphuric acid solution, but showed that quantitative hydrolysis could be obtained by boiling with a solution of sulphur dioxide in dilute acid solution. By this method there is substantial co-hydrolysis of titanium, tungsten and, to a lesser extent, molybdenum, but none of these elements prevents a quantitative yield of niobium and tantalum. Tungsten and molybdenum are subsequently separated by Powell, Schoeller

and Jahn's magnesia method[107] and titanium is corrected for by applying the hydrogen peroxide colour test to a solution of the final weighed oxide residue.

Cunningham's cupferron method may be applied directly to steel solutions, but it is really more suitable for ferro-alloys. For steels it compares unfavourably with the hydrolysis method in that an appreciable amount of iron is co-precipitated with the cupferron complex, whereas precipitates obtained by sulphurous acid hydrolysis are remarkably free from iron. With so much iron present in the cupferron precipitate a different finishing procedure is necessary. The mixed oxides are fused with potassium bisulphate, and iron is removed as ferrous sulphide from ammoniacal tartrate solution. Niobium, tantalum and titanium are then recovered as pure oxides by a second cupferron precipitation, and correction is made for titanium.

For the separate determination of niobium and tantalum, either directly or after separation as mixed oxides, several methods are available, but most of them are lengthy, involved and not always entirely satisfactory. They include fractional precipitation with tannin, volumetric determination of niobium after reduction with nascent hydrogen, chromatography and ion exchange or photometric methods based on selective colour reactions. Tantalum may also be determined by radioactivation analysis.[6]

Most of the early published work on separation procedures favours Schoeller's classical tannin method. The manipulation is very lengthy and involves the processing of a whole series of fractions varying from pure tantalum to pure niobium and repeated re-fractionation of the intermediate fractions. The method is much too slow for anything but occasional use. Nevertheless, it must still be regarded as the ultimate umpire procedure.

Volumetric methods based on reduction with nascent hydrogen, either with zinc-reductor columns or with liquid amalgams, are sometimes useful, but they are liable to give low results for niobium owing to partial hydrolysis resulting in the production of a colloidal phase that is not reduced with nascent hydrogen. Knowles and Lundell[108] made a critical assessment of this procedure and showed that under properly controlled conditions succinic acid could be used to inhibit hydrolysis during reduction and that calculated additions of titania, previously used by Cunningham,[105] could be dispensed with. Experience with this method for steels and ferro-alloys suggests that it is fairly satisfactory when niobium is the minor element and tantalum predominates, but less satisfactory when the order is reversed.

Separation by chromatography on cellulose has been an outstanding development and is now established as the best general-purpose works procedure for the analysis of ferro-niobium-tantalum, to which it can be applied directly. The method is primarily derived from the work of Burstall and co-workers[5,109] and Mercer and Williams,[110] and is based on the differential elution of the earth acid ammonium fluoro-salts through a cellulose column with mixtures of ethyl methyl ketone and hydrofluoric acid. The method gives accurate results. The main disadvantages are the toxic, inflammable and objectionable nature of the solvent and the time required. The column treatment results in large volumes of solution requiring a long evaporation treatment to obtain the pentoxides, as there is no reliable procedure for precipitating the niobium and tantalum directly from their respective solvent fractions. Wells[111] has described details of a simple paper-strip method for steel. The strips are spotted with an aliquot of the steel solution and suspended in the solvent (*iso*butyl methyl ketone *plus* 4 per cent. of hydrofluoric acid) for 20 to 40 minutes for diffusion to take place. Niobium gives a distinctive yellow band away from the dark iron colour at the bottom. Tantalum is similarly extracted, but by spraying with tannic acid only the niobium is coloured and there is no interference from tantalum. By reducing the hydrofluoric acid concentration of the *iso*-butyl methyl ketone to 2 per cent., niobium can be fixed near the original spot and tantalum, which alone moves in the solvent front, can be detected by spraying with quinoline.

Column separations with anion-exchange resins are coming into use. These are based on the work of Kraus and Moore[112] and Hague, Brown and Bright[113] with hydrochloric - hydrofluoric acid mixtures on Dowex I resin columns and Cabell and Milner[114] with the British resin De-Acidite FF. In applying these methods to steel, experience to date has suggested that they are by no means so satisfactory as the chromatographic method, and further detailed investigation is necessary before the multiple-elution sequence necessary to provide for niobium, tantalum, molybdenum, tungsten and titanium can be properly controlled.

Of the few available colour reactions that can be used as photometric procedures, the thiocyanate reaction for niobium and the pyrogallol reaction for tantalum appear to be the best, although both have inherent limitations. The niobium thiocyanate colour is developed

in moderately strong acid in the presence of a reducing agent (stannous chloride) and can be selectively extracted with a variety of solvents including diethyl ether, ethyl and *iso*amyl acetates and *cyclo*hexanol. Of these, diethyl ether appears to be the best. Freund and Levitt[155] develop the colour in a homogeneous aqueous system after adding acetone, which minimises the dissociation of the complex and permits the optical density to be measured directly without solvent extraction. These conditions have been adapted by Milner and Smales[6] in a method for steel. The reaction conditions are extremely critical and require the most exacting standardisation, but more stable conditions have been formulated in a further modification by Bacon and Milner.[116]

The pyrogallol reaction has been described by Gots and Kakita[117] and more recently by Hunt and Wells.[118] The tantalum complex is developed in acid solution and the niobium complex in alkaline solution. Both complexes are yellow, and both obey Beer's law, but there is interference from a number of elements, in particular from titanium. Interference from titanium is the main factor preventing the general use of the method in steel analysis. The titanium colour reaction has about five times the sensitivity of the tantalum reaction and complete separation from this element is therefore essential. Attempts to achieve this by precipitation from a dilute sulphuric acid - tannin solution have proved reasonably satisfactory, but a trace of tantalum is lost in the process. The pyrogallol reaction can be applied ideally after a chromatographic separation, but this is a relatively lengthy process. Tungsten also interferes, but its effect can be largely suppressed with phosphoric acid.

Nitrogen

Nitrogen is usually determined either by the vacuum fusion method or by purely chemical methods based on quantitative conversion of the nitrides to ammonia. The results of a comprehensive study and comparison of the various methods have recently been published in an Iron and Steel Institute Special Report.[119]

The vacuum fusion method has no particular advantages over the chemical methods and is comparatively unsuitable for repetition work. Judged purely as a method for nitrogen it is hardly worth while, unless determination of oxygen or hydrogen is required simultaneously. It also suffers from the disadvantage that nitrogen is usually obtained by difference after determination of the other gases evolved and the results are therefore affected by the algebraic sum of the errors of the gas analysis. Statements that the vacuum fusion procedure gives nitrogen values 0·001 to 0·002 per cent. below those obtained by chemical procedures are refuted in the Special Report.

Chemical methods depend on conversion of the nitrides to ammonium salts by dissolution of the steel in mineral acid and subsequent liberation of ammonia, usually by distillation from sodium hydroxide. The ammonia is then determined titrimetrically with standard acid or colorimetrically with Nessler's reagent. Certain nitrides are very resistant to acid attack, for example, nitrides of aluminium, boron, chromium, titanium, vanadium and zirconium, and prolonged digestion with fuming sulphuric acid may be necessary for complete decomposition.

Differentiation between the various nitrides present in steel is not a practical proposition, but a method has been proposed by Beeghly[120] for the determination of aluminium nitride. This depends on the selective action of sodium hydroxide, in which most other nitrides are completely insoluble. The steel is first decomposed in a mixture of bromine and methyl acetate, which leaves a residue of unattacked nitrides, oxides and other non-metallic compounds. The residue is then digested with sodium hydroxide and the ammonia released by the decomposition of the aluminium nitride is determined by the usual methods.

Oxygen

The vacuum fusion process[71] is the most reliable method for determining oxygen and this technique can be used for all types of steel. Improvements in the design of the apparatus, dependent on the method of heating—either resistance[121] or high frequency[122]—have been the main developments in recent years. Conventionally, the oxygen is determined gas volumetrically as carbon monoxide, along with hydrogen and nitrogen, but in Speight and Cook's method[121] the carbon monoxide is converted to carbon dioxide, which is isolated from the other gases by freezing, and afterwards re-gasified and its volume measured. A promising new technique[123] utilises a carrier-gas principle instead of a vacuum pump to remove the gases

from a fusion apparatus otherwise similar in construction to the one used for fusion in vacuum. The carbon monoxide is converted to carbon dioxide and determined gravimetrically in a similar manner to the determination of carbon in steel.

Methods for determining oxygen in steel by purely chemical procedures are comparatively limited in scope and are mainly restricted to plain and low-alloy steels. A chlorination technique has been used[124] in which the metallic elements are converted to volatile chlorides in an atmosphere of chlorine, leaving a residue of oxide inclusions, which is analysed for its individual components and the oxygen content computed from the results. Methods based on separation of the oxides by dissolution of the steel in alcoholic iodine have been used for many years and have been reviewed recently by Garside, Rooney and Belli.[125] Another method depends on conversion of the oxides to alumina[126] by heating thin samples of steel between strips of aluminium in vacuum at 1250° C. Aluminium diffuses into the steel and reacts with the oxides present to form alumina, which is determined in the insoluble residue after dissolving the steel in mineral acid. Older methods based on the formation of alumina in the liquid steel are still practised as a means of determining the oxygen content during the melting process. In these methods, based on the original Herty technique, a spoon sample of the liquid steel is "killed" with an excess of aluminium and the alumina produced subsequently determined in the acid-insoluble residue. The results are only approximately correct and the degree of error may vary widely depending on the type of steel, solubility in acid, nature and concentration of the acid used and the time required for extraction. In general the method is only suitable for plain carbon and simple alloy steels.

Phosphorus

The most widely used method for the determination of phosphorus depends on precipitation as ammonium molybdophosphate and then alkalimetric titration or conversion of the molybdenum equivalent to lead molybdate and gravimetric determination. Alkalimetric titration is almost invariably used in general works practice when speed is an over-riding consideration, but for umpire determinations, the gravimetric method is much to be preferred. Methods based on direct weighing of the molybdophosphate are seldom practised in steel analysis, mainly because the precipitate cannot be collected on filter-paper for this purpose and also because of the critical nature of the drying temperature on the composition of the precipitate. Conversion to magnesium pyrophosphate has the advantage of being independent of variations in the ratio of phosphorus to molybdenum in the precipitate, but it is otherwise comparatively insensitive and requires expert manipulation to ensure quantitative precipitation of the small amounts of phosphorus usually found in steel.

The molybdophosphate reaction is critically affected by many variables, such as acidity, temperature, molybdic acid concentration, phosphorus concentration, time of standing, stirring and the effect of other elements, *e.g.*, arsenic, vanadium, titanium, tungsten, zirconium, niobium and tantalum, which interfere either by partly inhibiting precipitation or by co-precipitation as related heteropoly compounds. A further difficulty is that some of these variables are so critically interdependent that it is almost impossible to devise conditions that are ideal or even suitable in all circumstances over the full range of phosphorus contents found in iron and steel.

The conditions for precipitation as molybdophosphate were first reviewed by Hundeshagen[127] and recently by Stockdale,[128] who gives a comprehensive survey of the reaction. Stockdale considers that the nitric acid concentration and the excess of molybdic oxide are the most important factors governing the precipitation of phosphorus from ferric solutions. Precipitates true to formula are obtained with a high nitric acid concentration and a minimum excess of molybdic oxide, but the yield is incomplete. With low acidity and high molybdic oxide concentration all the phosphorus is precipitated, but the compound carries an excess of molybdic oxide. He recommends precipitation with an excess of molybdic oxide to ensure a full yield of phosphorus, and then dissolution of the precipitate, removal of molybdenum as sulphide and re-precipitation of the molybdophosphate under ideal conditions in the absence of iron. This method gives excellent results, but it is too slow for general works routine.

The first of the two British Standard methods for steel[129] is not entirely satisfactory, as the acidity is critically dependent on the analyst's judgment and manipulation, and may vary widely with different operators; the general tendency is towards positive error from co-precipitation of excess of molybdic oxide. The second British Standard method,[130,131] based on precipitation from perchloric - nitric acid solution, has virtually made the older method

redundant, as the precipitation conditions can be controlled more precisely, provision is made for all interfering elements and the method can, therefore, be applied to all types of steel.

Methods in which perchloric acid is not used have a much more restricted scope and are in the main limited to steels soluble in dilute nitric acid. Such methods have not changed much in essentials since the original Handy method on which they are based, and, on account of their simplicity, they are still used extensively in general works practice.[132] There may be interference from un-decomposed carbides, particularly with high-carbon chromium - molybdenum steels, and from arsenic and vanadium. Interference from arsenic is not serious for steels containing $< 0{\cdot}03$ per cent. of the element and can be controlled by reducing the precipitation temperature to $< 40°$ C or by using a high nitric acid concentration. Removal as tribromide, recommended in the British Standard perchloric acid method, is not readily applicable in a direct nitric acid method. Interference from vanadium can also be controlled by using a high nitric acid concentration or by reduction with sulphurous acid to the vanadyl condition before the molybdophosphate precipitation. Precipitation of phosphorus from a high nitric acid concentration is relatively slow and may be incomplete with low-phosphorus steels. Precipitation may be accelerated by raising the temperature to above 70° C, but this increases the risk of interference from arsenic and may lead to co-precipitation of excess of molybdic oxide. Vigorous shaking is necessary to induce precipitation and this may also result in co-precipitation of molybdic oxide, particularly with high-phosphorus steels. If no provision need be made for arsenic, reduction with sulphurous acid is preferable to a high nitric acid concentration as a means of controlling interference from vanadium.

Colorimetric methods are used based on reduction to molybdenum blue,[1] but the reaction is sensitive to minor variations in conditions and results are not very reproducible in general routine practice. The phosphovanadomolybdic acid colour reaction is much to be preferred. According to Kitson and Mellon[133] the yellow colour of the phosphovanadomolybdate can be measured directly in solutions of simple steels, but Elwell and Wilson[134] showed that the colour could not be measured accurately in the presence of iron, chromium or nickel and recommended solvent extraction with *iso*amyl alcohol, in which the compound is selectively soluble. The method is much quicker in operation than the classical gravimetric methods and gives reliable results for a wide range of steels, including high chromium - nickel stainless steels and tungsten high-speed steels. There is minor interference from arsenic and for accurate work it is recommended that this element should be removed as the tribromide.[135]

Silicon

Silicon is usually determined gravimetrically after dehydration of silicic acid to insoluble silica with mineral acids or photometrically by methods based on the molybdosilicic acid colour reaction.

In the gravimetric methods the dehydration may be made by baking a hydrochloric or hydrochloric - nitric acid solution of the steel or by heating to fumes with sulphuric or perchloric acid. Of these, perchloric acid is the most effective and is used in the recommended British Standard method for steel.[136] By this method, only about 0·5 mg of silica remains in solution after a single dehydration treatment, equivalent to 0·005 per cent. of silicon when the factor weight of sample, 4·67 g, is used. Double dehydration to recover the trace of remaining silicon is, therefore, only necessary for the most exacting requirements. Dehydration with sulphuric or hydrochloric acid may leave as much as 2 mg of silica in solution after a single treatment. Fowler[137] investigated the dehydration efficiency of various acids; with a 2·336-g sample of 4·7 per cent. silicon steel he found that one dehydration with sulphuric acid left from 1·8 to 2·3 mg of silica in solution. With double dehydration the soluble silica was reduced to an average value of 0·65 mg. Dehydration is also more difficult to control with sulphuric acid, as the sulphates deposited during the later stages of the evaporation are apt to cause spirting and bumping of the solution, and salts projected on to the beaker cover in this way may not be fully dehydrated. The fumed concentrate is also more difficult to extract, as basic sulphates may be formed that are not readily re-dissolved, whereas the corresponding perchlorates are freely soluble in acids or water. Dehydration with hydrochloric acid is easier to handle than that with sulphuric acid, but its use is limited to comparatively simple steels unless nitric acid is also added to decompose carbides.

Perchloric acid has a much wider range of application than have the other acids, as its use permits the effective decomposition of complex alloy carbides in highly alloyed steels, yielding silica residues remarkably free from contamination. Titanium salts are also freely

soluble in perchloric acid extracts, and residues from steels containing up to 1 per cent. of titanium show only minor contamination. With hydrochloric acid dehydration there is always extensive hydrolytic precipitation of titanium, sometimes as much as half the titanium present being precipitated in this way. Dehydration with phosphoric acid is sometimes used for steels high in tungsten, as this "fixes" the tungsten as soluble phosphotungstate and thus prevents the co-precipitation of tungstic acid. This method is not entirely satisfactory, as soluble phosphosilicic acid complexes that are difficult to dehydrate may be formed and hot concentrated phosphoric acid attacks glassware very severely. High and variable results may therefore be obtained unless the dehydration is carried out in Vitreosil-ware.

Acid-resisting high-silicon irons containing 10 to 18 per cent. of silicon require a specialised dissolution treatment. In the recommended British Standard method[138] for silicon iron the sample is dissolved in a mixture of ammonium chloride, bromine and hydrobromic acid and dehydrated by evaporation to dryness over a steam-bath. About 2 mg of silicon remains in solution after this treatment and is recovered by dehydrating the filtrate with perchloric acid.

The presence of milligram amounts of oxide impurities in silica residues does not usually cause much trouble, as the determination is completed by measuring the loss in weight when the silica is volatilised as tetrafluoride. Errors may arise owing to change in composition of the residual oxides after the hydrofluoric acid treatment or to the retention of sulphates if sulphuric acid is also used to prevent volatilisation of titanium and other fluorides. For these reasons the non-siliceous residue should be kept as small as possible, preferably not exceeding 5 mg, but this is a counsel of perfection that cannot always be achieved, as substantial contamination may be unavoidable if niobium, tantalum, tungsten or molybdenum is present. Tungstic and molybdic oxides are slowly volatilised at ignition temperatures exceeding 800° and 550° C, respectively, and may cause significant error if the ignition is prolonged above these temperatures after the hydrofluoric acid treatment or by incomplete conversion of sulphates to oxide if the ignition is made at lower temperatures. Separation from tungstic and molybdic oxides by fusion with sodium bisulphate and re-precipitation of silica after extraction in citric, tartaric or oxalic acid is not altogether successful, as small amounts of silica are also extracted.

Colorimetric methods are now used extensively, particularly for works routine purposes. The silicon is first converted to the yellow-coloured molybdosilicic acid, which is then reduced to molybdenum blue and measured photometrically. By suitably regulating the acid concentration the molybdosilicic acid can be selectively reduced in the presence of phospho-, vanado- and arsenomolybdate. Compensation for the inherent colour of other alloying elements is made by a difference reading against a similar solution in which the molybdosilicic acid reaction is inhibited by altering the sequence of acid and reagent additions. The reduction to molybdenum blue can be made with a variety of reducing agents, of which stannous chloride[2] or a combination of ferrous sulphate and oxalic acid[139] is preferred. Both these methods of reduction are incorporated in British Standard methods, the former in a method for general application up to 2 per cent. of silicon[140] and the latter in a sensitive short-range method for steels containing $< 0{\cdot}05$ per cent. of silicon.[141] The main difficulties experienced with molybdosilicic acid methods are the critical response of the reaction to minor changes in acidity, reagent concentration and temperature, impure reagents, and blank pick-up from storage of solutions in glassware. It should also be noted that the method of dissolution limits the application of the method to comparatively simple steels soluble in 5 per cent. sulphuric acid and that only elemental silicon is determined. Silica and silicate inclusions present in the steel are not decomposed and hence are not determined by the method. This sometimes fulfils a useful purpose, as the gravimetric methods are non-selective in this respect and record the total silicon content irrespective of its state of combination.

Sulphur

Three methods in general use for determining sulphur are—(*a*) the gravimetric barium sulphate method, (*b*) high-temperature combustion in oxygen and alkalimetric or iodimetric titration of the evolved sulphur gases, and (*c*) evolution as hydrogen sulphide and iodimetric titration.

The gravimetric procedure is still the primary method, but it is not extensively used in routine practice owing to the time factor and the relatively high degree of skill required to

operate it successfully. Its use is mainly restricted to referee determinations and the preparation and checking of control standards for the combustion process, which is now the recognised works routine procedure. The hydrogen sulphide evolution method has been virtually superseded by the combustion procedure. Evolution of hydrogen sulphide is not always quantitative; full recovery is dependent on the metallurgical condition of the steel and the presence or absence of elements, such as copper or molybdenum, that "fix" sulphur in the solution and prevent its evolution as hydrogen sulphide. However, for certain steels of simple composition and when the metallurgical condition of the sample is closely reproducible, the method still has certain advantages. For example, whereas an individual determination may take rather longer than the combustion process, it is possible to operate the method in batteries of up to 10 tests or more. The average time per test is then very much in its favour and this can be an important point when several casts are being refined simultaneously.

The gravimetric barium sulphate method is not by any means an ideal procedure, in spite of its acknowledged status as the primary reference method. The baking treatment to expel residual nitric acid and decompose ferric nitrate is difficult to control. Insufficient baking gives low results owing to incomplete destruction of nitrates, and over-baking also results in loss of sulphur owing to formation of insoluble basic iron and chromium compounds. The conditions are so critical, particularly with steels of high chromium content, that there is often no controllable margin between error from retained nitrates and error from basic salt formation. Basic salts also tend to pass through the filter in colloidal form and subsequently contaminate the barium sulphate precipitate. A further effect of chromium is that it tends to form chromo-sulphuric acid complexes of low ionic dissociation, with the result that some of the sulphur may not be precipitatable with barium sulphate. Complete precipitation is also difficult to achieve with very low sulphur steels ($< 0{\cdot}015$ per cent.) and various devices are used to speed the precipitation, for example, the addition of known amounts of a standard sulphur solution. The method also suffers from inconsistent blanks and the fact that blanks determined on a pure solution of the reagents are not strictly comparable with the test conditions, which are modified considerably by the presence of ferric chloride and other salts.

Bagshawe and Pill[142] eliminated the critical baking treatment altogether and used hydroxylamine hydrochloride to destroy residual nitrates; this has considerably simplified the operational technique and has led to much improved results on chromium steels. The hydroxylamine treatment is incorporated in the revised British Standard procedure.[143] Nydahl[144] separates the sulphur from interfering ions by selective chromatographic adsorption on aluminium oxide before precipitating with barium chloride, whereas Belcher, Gibbons and West[145] remove iron by extraction with *iso*amyl acetate and subsequently determine the barium sulphate titrimetrically with EDTA.

The combustion process by virtue of its speed and simplicity has now become firmly established as a works routine method. The results are highly reproducible, but have to be computed empirically with relation to steels of known sulphur content, as the combustion reaction is not stoicheiometric. Lack of stoicheiometry appears to be related to the formation of an equilibrium mixture of sulphur dioxide and sulphur trioxide with incomplete recovery of the sulphur trioxide fraction on account of (*a*) incomplete adsorption of sulphur trioxide mist, and (*b*) condensation in the cooler parts of the tube and exit system. The latter may be caused by the presence of traces of moisture or by entrained ferric oxide dust. Ferric oxide is an active catalyst for sulphur trioxide formation and at low temperatures, 400° to 500° C, sulphur may be fixed as ferric sulphate in the cool end of the tube. The proportion of sulphur trioxide in the combustion gases diminishes progressively with increasing temperature and a high operational temperature is, therefore, of paramount importance. If working temperatures approaching 1600° C could be achieved, it is proable that the yield factor would come extremely close to the theoretical value. As it is, the average yield is rarely better than about 90 per cent. and may drop to as low as 80 per cent. as the tube becomes progressively fouled with deposited oxides and slag adhesions.

The elimination of all filters and plugs of asbestos, cotton-wool, etc., and the simplification of the delivery part of the system has been an important trend.[146] This has been made possible by pre-heating the sample in the hot combustion zone before admitting oxygen. Preheating causes the charge to frit or sinter and when combustion takes place after admission of oxygen, there is practically no entrainment of ferric oxide dust with the exit gases. This is particularly important with high-carbon steels and pig or cast irons with which the evolution

of carbon dioxide results in heavy "carry over" of ferric oxide, which fouls the exit tubes and reduces the sulphur yield by holding sulphur gases in the cooler parts of the system.

Hydrogen peroxide is preferred to silver nitrate as the absorbing medium, as the titration can be made in a clear solution. With silver nitrate, the titration must be made in the presence of precipitated silver sulphite. Sodium borate is now considered a better titrant than sodium hydroxide. Its most important feature is that it permits the procedure to be used successfully on high-molybdenum steels. Molybdic oxide carried over in the gas stream reacts with strong alkalis and therefore interferes when the titration is made with sodium hydroxide, but it does not readily react with sodium borate unless a large excess is used. Steels containing up to 16 per cent. of molybdenum can be analysed without interference. The alternative method, depending on absorption of the gases in water and titration with iodate, is generally less satisfactory than the alkalimetric titration, as only sulphur dioxide is determined and the percentage yield is, therefore, appreciably lower.

Tin

The usual method of determining tin is based on reduction to the bivalent condition with a metallic reductant and then titration with standard iodine or iodate. The reducing metal may be antimony, aluminium, iron, nickel or lead, used singly or in suitable combinations.

Reduction with nickel in the form of an etched or activated spiral is probably the most exact, but reduction is slow and the green colour resulting from dissolved nickel tends to impair end-point sensitivity. Metallic antimony as a finely ground powder is the quickest reductant, but its use has been severely criticised by Evans and Higgs[147] and others. The objection to antimony is that the accuracy of titration is a critical function of antimony particle size; a coarse antimony gives low results owing to incomplete reduction, whereas a finely ground flour gives high results owing to reaction with iodine. Thus, high or low results may be obtained at will, mainly by altering the grading of the antimony flour, and correct results are largely a matter of chance. This source of error can be largely overcome by a combination of metallic aluminium and a dissolved antimony salt. This results in the precipitation of metallic antimony in a state of uniform and reproducible fineness and hence of uniform chemical reactivity. If repeated aluminium additions are made until a slight excess of antimony persists in the boiling solution, complete reduction of tin is certain and the very small amount of residual antimony incurs no measurable error. Results have also been put forward indicating loss of tin in the antimony residue; according to Evans, as much as 25 per cent. of the tin present. This is certainly not true for the very low concentrations of tin involved in steel analysis and does not arise when the combined aluminium - antimony salt method is used, as only traces of residual antimony remain out of solution.

For irons and low-alloy steels, the method may be applied directly to a solution of the sample in hydrochloric acid.[148] Some steels give fading end-points by the direct method, presumably owing to reaction of iodine with carbon compounds. This tendency can be largely eliminated by a treatment with hydrogen peroxide before reducing the tin.

The direct method is not suitable for highly alloyed steels owing to the difficulty of locating the end-point in the presence of coloured salts, *e.g.*, salts of chromium, nickel, or cobalt, or on account of the chemical interference of large amounts of tungsten or copper. Tungsten cannot be separated as tungstic acid because it occludes tin. It is best removed as unattacked stable carbide or tungstide after dissolving the steel in a non-oxidising acid. Tungsten carbide residues are dense and tractable and do not adsorb tin. The filtrate from the carbides is directly suitable for precipitation of tin as sulphide, which serves to isolate it from interfering elements preparatory to reduction and titration.

The response of trace amounts of tin to precipitation as sulphide is apt to be erratic and recoveries are generally low. This appears to be due to the absence of sufficient precipitate-forming nuclei, but by co-precipitating the tin on a carrier sulphide, molybdenum or copper, a quantitative yield can be obtained.[149] Molybdenum is preferred to copper as the carrier sulphide, as copper tends to interfere with the iodine titration. The method is applicable to all types of alloy steel.[150,151]

Colour methods for tin are rarely used in steel analysis, but the element can be determined polarographically either directly or after separation from the steel solution. Direct polarography is suitable for high tin contents, but for the more usual trace amounts, the element must first be separated as sulphide or by co-precipitation on manganese dioxide. Tin,

together with antimony, molybdenum and several other elements, is quantitatively co-precipitated when manganese dioxide is precipitated with bromate from nitric acid solution.[152]

Titanium

Titanium is usually determined photometrically by the hydrogen peroxide reaction, either directly in the steel solution or after separation of titanium from interfering elements. In the simplest case, the peroxytitanyl compound is developed directly in a sulphuric acid solution of the steel and requires no separation from chromium, nickel or other elements forming coloured salts. The optical density is then measured relative to a blank or compensating solution prepared from the steel itself.[153] In this way the inherent colour of foreign ions is exactly compensated for. The only elements interfering are vanadium and molybdenum, both of which give coloured reaction products with hydrogen peroxide. The molybdenum colour is comparatively insensitive, *e.g.*, 3 per cent. of molybdenum is equivalent to 0·05 to 0·10 per cent. of titanium, depending on acidity and other conditions, but the relationship is strictly proportional under defined conditions and can be corrected for if the molybdenum content is known. The vanadium colour is of comparable sensitivity to the titanium colour and the direct method cannot therefore be applied. The method of applying it, based on the difference reading between the colours of the test solution and a similar blank solution, in which the titanium colour reaction is inhibited by the addition of fluoride,[154] is not recommended for precise work, as fluorides modify the inherent blank colour.

When separation is needed to eliminate interfering elements, various procedures can be adopted, including precipitation with cupferron from reduced (ferrous) solution, hydrolysis from dilute acid solution with sulphur dioxide, sodium thiosulphate or phenylhydrazine, precipitation with *p*-hydroxyphenylarsonic acid from dilute hydrochloric acid solution. None of these is entirely satisfactory, but cupferron is the one most frequently used and forms the basis of the recommended method for steel.[155] Precipitation with cupferron eliminates most of the iron and elements, such as chromium and nickel, having coloured salts. Vanadium is co-precipitated, but if it is reduced to the quadrivalent state with an excess of sulphur dioxide just before adding the cupferron, the contamination is of a very minor order. Further separation, however, is necessary for vanadium alloy steels, for example, by fusing the ignited cupferron residue with sodium carbonate and precipitating the titanium as metatitanic acid by boiling the aqueous extract. In addition to vanadium, this also eliminates any molybdenum or tungsten carried down with the cupferron precipitate. The titanium precipitate is then ignited, fused with potassium bisulphate and the hydrogen peroxide reaction applied to the acidified fusion extract. If the sodium carbonate separation stage is omitted, interference from residual traces of vanadium can be prevented by adding a few drops of 0·5 per cent. hydroxymaleic acid solution before adding the hydrogen peroxide.

The peroxide reaction can be developed in dilute sulphuric acid, phosphoric - sulphuric acid mixture or in acid citrate, tartrate or oxalate solution. Acid citrate or tartrate is recommended for complex highly alloyed steels, as interference from the hydrolytic precipitation of niobium, tantalum or tungsten is prevented if the potassium bisulphate melt of the mixed oxides is extracted directly in citric or tartaric acid. Citric acid is specified in a recent method recommended by the B.I.S.R.A. Methods of Analysis Committee.[156] The peroxytitanyl colour is modified by variations in acidity, particularly of phosphoric acid, which reduces the sensitivity, but also to a lesser extent by sulphuric, citric or other acids that may be present. It is essential, therefore, that test and calibration conditions should be closely correlated. The colour is extremely sensitive to traces of fluoride, which have a pronounced bleaching action, and, because of this, treatment of siliceous residues with hydrofluoric acid should always be avoided.

Titanium may also be determined by the hydrogen peroxide method after solvent extraction of iron, vanadium and other elements as the carbamates with pyrrolidine - dithiocarbamate in chloroform.[157] This method offers a simple approach to the problem of vanadium interference, as up to 4 per cent. of vanadium can be selectively extracted in this way.

For the determination of traces of titanium, sufficient sensitivity for most purposes can be obtained by the cupferron method with 5 or 10-g samples. Alternatively, iron, chromium, nickel and other elements can be separated from 10-g samples by mercury-cathode electrolysis and titanium determined in the residual electrolyte. By this means from 0 to 0·025 per cent. of titanium can be determined with an accuracy to within $\pm 0{\cdot}001$ per cent.

The reagent 1:2-dihydroxybenzene-3:5-disulphonate (tiron)[158] is more sensitive than hydrogen peroxide for trace determinations. The titanium must be separated from most of the iron, but the colour from residual small amounts of iron can be bleached with sodium dithionite in the pH range 4·3 to 5·0. Vanadium and molybdenum interfere and the reaction conditions are critical.

Gravimetric and volumetric methods are rarely used for steel analysis. The British Standard gravimetric method for permanent-magnet alloys[159] is applicable to steels and depends on precipitation with cupferron, separation of residual iron as ferrous sulphide from ammoniacal tartrate solution, precipitation with cupferron and ignition to oxide. The method is accurate if niobium, tantalum and zirconium are absent. Volumetric methods, based on reduction with nascent hydrogen, are not sufficiently specific to have any worthwhile application in steel analysis.

Tungsten

The standard gravimetric method,[160] based on hydrolytic precipitation of tungstic acid, is recommended for steels containing more than 3 per cent. of tungsten. For lower tungsten contents, separation by hydrolysis is uncertain and liable to be incomplete. Below about 0·5 per cent. of tungsten, the results are erratic and below about 0·1 per cent., precipitation may fail altogether.

Various auxiliary precipitants have been recommended to improve the yield, for example, cinchonine and rhodamine B,[161] but without complete success, and it is noteworthy that most of the reagents recommended lead to increased co-precipitation of molybdenum. The degree of molybdenum contamination occurring is influenced by a variety of factors, *e.g.*, the acidity of the solution, the time allowed for precipitation, the concentration of the two elements and the ratio of their respective concentrations. Conditions favouring a quantitative yield of tungstic acid always favour an increase of molybdenum contamination. Thus, minimum acidity, reduction of the iron with sulphurous acid, use of auxiliary organic precipitants and long standing before filtration all tend to improve the yield of tungstic acid, but usually at the expense of increased contamination from molybdenum, vanadium and other elements. Tungstic oxide residues from 2-g samples of high-speed steel (6 per cent. of tungsten - 6 per cent. of molybdenum) may contain anything from 10 to 25 mg of co-precipitated molybdic oxide. The accurate determination of residual molybdenum in the tungstic oxide is, therefore, an important consideration. Milligram amounts of vanadium, chromium and iron may also be co-precipitated, and a general charge against steel-industry chemists is that they often oversimplify tungsten determinations and do not make proper allowance for impurities.

In addition to cinchonine and rhodamine B, other organic precipitants that have found some use include Yoe's reagent,[162] antipyrine (phenazone), tannin and various benzidene derivatives. Yoe's reagent is the equal of cinchonine as a precipitant, but it also induces substantial co-precipitation of molybdenum. Antipyrine, recommended by Moser and Blaustein,[163] is also equal to cinchonine, but the precipitates are bulky and sticky and difficult to filter and wash. From a manipulative point of view cinchonine and rhodamine B are both better than antipyrine. Belcher and his co-workers have made a systematic study of benzidene and related compounds and amongst these 4:4′-diaminostilbene[164] was found to precipitate tungsten and molybdenum quantitatively from neutral solution. In applying the reagent to steel, interference from molybdenum can be suppressed completely by precipitating from 0·7 *N* hydrochloric acid, but the tungsten yield is also slightly impaired.

In view of all the inherent difficulties associated with precipitation methods, probably the most accurate procedure is to recover most of the tungsten by simple hydrolysis from fairly strong acid solution, *e.g.*, 15 to 20 per cent. hydrochloric acid, thus ensuring the minimum of contamination, and then to determine the small amount of unrecovered tungsten by one of the colour reactions. Below about 3 per cent. of tungsten, the colour methods can be used to supersede the hydrolysis procedure.

The most accurate colorimetric method is the one based on the reaction with toluene-3:4-dithiol.[165] Molybdenum gives a corresponding colour with dithiol, but it can be preferentially developed in cold weak acid solution and selectively extracted with amyl acetate before developing the tungsten colour in a hot solution of increased acidity. Under these conditions the reaction is specific for tungsten in steel.

Methods based on the tungsten thiocyanate colour have been used extensively in recent years, but they seem to have presented a curious mixture of hope fulfilled and hope deferred.

The reaction is critically affected by variation of conditions and the most exacting and rigid standardisation is necessary. The colour is developed at a much higher acidity than is used in the corresponding molybdenum method, but complete suppression of the molybdenum reaction has been one of the main problems. The B.I.S.R.A. Methods of Analysis Committee[166,167] recommends a combination of titanous and stannous chlorides as the reducing agent and has shown that up to 3 per cent. of molybdenum can be tolerated without interference. This has been modified in the British Standard method,[168] which provides for up to 1·5 per cent. of molybdenum. Vanadium interferes by forming a similarly coloured compound, but of relatively low sensitivity. The interference is not completely independent of tungsten, probably owing to the formation of complex acids, but no serious error is introduced by making a linear correction for vanadium below about 0·3 per cent. The specified range for the standard method is 0 to 3 per cent. of tungsten, but if some loss of accuracy can be tolerated the range can be extended considerably. By suitable reduction of sample weight, steels containing up to 24 per cent. of tungsten can be accommodated and high-speed steel containing 18 per cent. of tungsten can be analysed with an error of about $\pm$0·3 per cent. In the recommended standard range, 0 to 3 per cent. of tungsten, the average reproducibility is about $\pm$0·03 per cent. Although it is not as accurate as the toluene-3:4-dithiol procedure, the method has decided advantages for repetition work in routine practice.

Vanadium

The best methods for steel are based on the titrimetric measurement of the V_2O_4 to V_2O_5 transformation. The titration can be made in either direction, *i.e.*, by titration of quinquivalent vanadium with a standard reducing agent, such as ferrous sulphate, or by measured oxidation with standard permanganate after reduction to the quadrivalent state with sulphur dioxide, hydrogen sulphide or ferrous sulphate. Excess of sulphur dioxide or hydrogen sulphide must be removed by boiling, and excess of ferrous sulphate can be selectively oxidised in cold solution with ammonium persulphate. Sulphur dioxide and hydrogen sulphide can only be applied after a separation of iron, as this element is also reduced, but reduction with ferrous sulphate can be applied directly to a steel solution. For convenience in routine practice it is often combined with a determination of chromium, the titration being carried out after completing the chromium test by either the Vignal or persulphate procedures.

If vanadium alone is being determined it is preferable to oxidise with permanganate in cold solution to the quinquivalent condition and titrate with ferrous sulphate. This is the principle used in the recommended British Standard method.[169] An excess of permanganate must be used to ensure complete oxidation, after which sodium nitrite is added to reduce the excess, followed by sulphamic acid[170] to destroy residual nitrite. Urea may also be used. The titration end-point with diphenylamine is improved by the presence of phosphoric or hydrofluoric acid and both serve the additional function of complexing tungstic acid. The choice between them is a close one, but on balance the evidence is in favour of hydrofluoric acid.[171] There is some difference of opinion as to whether it is preferable to titrate with ferrous sulphate to the reduced form of the diphenylamine indicator, as in the British Standard method, or whether to use an excess of ferrous sulphate and back-titrate to the oxidised form with potassium dichromate. The advantage either way is a fine one, and it is mainly a matter of personal preference. Potentiometric titration by a dead-stop end-point procedure[172] is also satisfactory, and, although it is generally no more accurate than the visual method with diphenylamine, it has obvious advantages for highly alloyed steels for which the deep-green colour of the chromium - nickel salts interfere with the visual method. Amperometric titration with ferrous sulphate with use of an H-type polarographic cell and a rotating platinum electrode has also been recommended.[173]

With highly alloyed steels, separation from chromium can be made by volatilising most of the chromium as chromyl chloride from perchloric acid solution or from a mixture of perchloric and phosphoric acids if tungsten is present. Vanadium can also be precipitated with cupferron and in this way separated from large amounts of iron, chromium, nickel, etc. Separation of these elements by mercury-cathode electrolysis is also a useful preliminary treatment and can be carried out on comparatively large sample weights, *e.g.*, 5 to 10 g. It is, therefore, an excellent means of concentrating traces of vanadium preparatory to a colorimetric finish.

Alternatively, the vanadium in the residual electrolyte can be titrated under ideal conditions by the conventional methods.

There are only one or two colorimetric methods in general use. The oldest of these is based on the brownish yellow pervanadate colour produced with hydrogen peroxide. The reaction is somewhat limited in sensitivity and is affected by variation in acidity and by the background colour of chromium, nickel, iron and other coloured salts. Iron salts can be decolorised with phosphoric acid, but at the expense of some loss of sensitivity in the vanadium reaction. Titanium and molybdenum interfere directly by forming coloured peroxy salts, and tungsten interferes by forming phosphovanadotungstic acid. Interference from titanium can be prevented by adding hydrofluoric acid, which selectively bleaches the titanium peroxy compound. The method is useful for carbon and simple alloy steels with which interference is at a minimum and can be controlled. It is not very satisfactory for direct use on high-alloy steels, but it can be applied with good results after a mercury-cathode separation or after a preliminary separation of the vanadium with cupferron. The complex colour reaction between vanadium and tungstic acid in phosphoric acid solution offers the basis of a potentially better method. The structure of the complex is uncertain, but it is probably a co-ordinated compound of the heteropoly type with a partial replacement of the W_2O_7 groups in the phosphotungstate with V_2O_6 groups. It was first used in a method for steel by Wright and Mellon,[174] but has been improved recently by Scholes.[175] Scholes also examined the colour reaction with 3:3′-dimethylnaphthidine, previously recommended by Milner and Nall[176] for a micro method for steel, but found it less satisfactory than the phosphovanadotungstic acid method.

Zirconium

Methods based on hydrolysis separation from dilute acid solution with sulphur dioxide or sodium thiosulphate, or on precipitation as phosphate, have been used for many years. More recent methods depend on precipitation with cupferron, *n*-propylarsonic acid and other arsonic acids, selenious acid, mandelic acid and halomandelic acids. In these methods the element is determined gravimetrically, it being obtained and weighed as the oxide or converted to the phosphate.

The phosphate method is fairly specific, as quantitative precipitation can be obtained from solutions containing up to 10 per cent. by volume of sulphuric acid, from which only titanium, niobium, tantalum and tin are co-precipitated. Precipitation of titanium can be completely prevented by converting to the peroxytitanyl compound with hydrogen peroxide, and this reagent also considerably reduces the contamination from niobium and tantalum. Precipitation of small amounts of zirconium is comparatively slow, particularly in the presence of iron, but may be accelerated by the addition of titanium to act as carrier. This necessitates further separation, but it provides a useful means of collecting traces of zirconium from solutions obtained by dissolving 50 to 100 g of steel. The charge often levied against the phosphate method is that the precipitate undergoes partial hydrolysis during washing and may on this account contain rather less than the theoretical amount of phosphorus pentoxide for the pyrophosphate (ZrP_2O_7). The argument rests on a doubtful premise and is not supported by conclusive evidence. What evidence there is may well have been deduced from experiments in which zirconia of doubtful purity was used. The phosphate method described by Westwood and Mayer[177] is satisfactory for iron and steel.

Precipitation with cupferron from ferrous solution separates zirconium from chromium, nickel and most of the iron, but titanium, niobium and tantalum are quantitatively co-precipitated and there may also be contamination from vanadium, molybdenum and tungsten. In a recommended form of the method[178] the ignited oxides are fused with potassium bisulphate, the residual iron is removed as ferrous sulphide from ammoniacal tartrate solution and the zirconium is re-precipitated with cupferron. Precipitation as phosphate may also be applied as an alternative finishing procedure after separating zirconium from most of the iron with cupferron.

Precipitation with selenious acid from dilute hydrochloric acid solution is fairly specific, but most of the iron must be removed. The method can be applied after cupferron precipitation or after solvent extraction of iron with ether or separation by mercury-cathode electrolysis. Precipitation with *n*-propylarsonic acid[179] requires a double precipitation to remove

iron. Tin, niobium and tantalum are co-precipitated, but tin can be removed from the oxide residue as the volatile iodide.

Precipitation with mandelic acid was investigated by Kumins[180], Hahn[181] and Mills and Hermon.[182] Oesper and Klingenberg[183] and Klingenberg and Papucci[184] claimed that *p*-bromo- and *p*-chloromandelic acids had the advantage that the precipitates could be washed with water and weighed unchanged as the halomandelates. According to Hahn and Baginski,[185] however, the composition of the halomandelate depends on the acidity at the time of precipitation. In applying the mandelic acid reaction to steel analysis most of the iron should be removed either with cupferron or by mercury-cathode electrolysis. Preliminary tests of a mandelic acid method[186] by the B.I.S.R.A. Methods of Analysis Committee have given promising results. Small amounts of titanium do not interfere, but tungsten must be separated by fusion with sodium carbonate, and further separations are required if niobium and tantalum are present.

For small amounts of zirconium, colorimetric methods have been recommended after preliminary separations from interfering elements. Westwood and Mayer[187] recommend the reagent *p*-dimethylaminobenzeneazo-phenylarsonic acid, which gives a soluble yellow compound on extracting the acid-insoluble precipitate with sodium hydroxide. Titanium interferes and must be corrected for. Hahn and Johnson[188] have obtained good results by spectrophotometric measurement of the chloroanilate complex in perchloric acid solution after separation of interfering elements by mercury-cathode electrolysis.

Small amounts of zirconium can be determined by solution spectrography after a chemical concentration treatment with cupferron.[12]

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Flame-photometric Determination of Iron, Copper and Cobalt in Cobalt Mattes and Concentrates

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A method is described for the rapid routine determination of from 1 to 50 per cent. of iron, from 0·1 to 25 per cent. of copper and from 1 to 15 per cent. of cobalt in some metallurgical products. Iron is extracted with a mixture of ethyl methyl ketone and chloroform and determined separately. A duplicate determination takes approximately 2 hours.

Dean and Burger[1] have shown that from 50 to 600 p.p.m. of iron can be determined by flame photometry. Dean and Lady[2] have used acetylacetone to extract smaller concentrations of iron, and Dean[3] has shown that, despite self-absorption effects, up to 300 p.p.m. of copper can be determined in the flame. Burriel-Martí and Ramírez-Muñoz have determined cobalt by flame photometry and state that the useful concentration range is between 100 and 1000 p.p.m.[4]

In view of these facts and of the time taken in the chemical analysis of cobalt mattes, whether by Young's rapid method[5] or by ion-exchange techniques, it was decided to attempt flame analysis with the minimum of preliminary sample preparation.

Recently, Mason and de Beer[6] have described a spectrographic technique for determining iron, copper and cobalt in concentrates. It is thought that the proposed method will be of value when a spectrograph is not available.

Experimental

Preliminary investigation was directed towards the selection of wavelengths at which minimum mutual interference would occur. It was expected that iron would interfere more or less seriously with the other elements, and this was found to be so, with the exception of the cobalt line at 387·4 mμ, when the concentration of iron was below about 150 p.p.m. In the absence of iron, no serious interference was noted at 387·4 mμ when 2500 p.p.m. of copper were added to between 100 and 1000 p.p.m. of cobalt. Similarly, the copper line at 324·8 mμ was free from interference when from 100 to 1500 p.p.m. of cobalt were added. The addition of 500 p.p.m. of nickel did not interfere with the determination of either cobalt or copper.

Investigation into the selective extraction of iron indicated that convenient and complete removal could be obtained with a (2 + 1) mixture of ethyl methyl ketone and chloroform when the sample solution was about 8 *N* in hydrochloric acid; this solvent mixture has the advantage of high density. No iron was detectable in the aqueous layer after extraction. As the burner fitted to the photometer was not suitable for burning a purely organic solvent, it was necessary to remove the solvent by evaporation and to dissolve the residue in dilute sulphuric acid. The line at 386·0 mμ was used to determine iron, as only slight self-absorption was observed up to a concentration of about 700 p.p.m.

Interference—

As concentrates contained about 3 per cent. of magnesium oxide, interference by magnesium was expected in the determination of both iron and cobalt, owing to overlapping band spectra in the 386-mμ region. Extractions were made from pure solutions of ferric chloride to which different amounts of magnesium had been added, and it was observed that about 50 per cent. of the magnesium content was co-extracted. In order to overcome the enhancement of iron emission caused by co-extracted magnesium, the (L — H) method of measurement was tried.

Background readings (H) were made at the base of the iron line at 386·7 mμ when the sample solutions were being aspirated, and the mean of these readings was subtracted from the mean of readings made at the iron peak at 386·0 mμ (L); the (L — H) method thus gave the total net luminosity due to iron. This value was checked against a calibration graph

prepared from values obtained in the same manner when aspirating appropriate dilutions of a stock ferrous sulphate solution. In this way, the presence of up to 10 per cent. of magnesium oxide in the original sample can be tolerated.

Aluminium, calcium, sodium, manganese and potassium are not appreciably co-extracted and so do not interfere in the determination of iron.

Band interference by magnesium with the cobalt line at 387·4 mμ is of the same order as that for the iron line at 386·0 mμ. The (L — H) method was again applied, the same background wavelength being used as in the iron determination. Satisfactory results were obtained in the presence of up to 10 per cent. of magnesium oxide in the original sample.

Aluminium was the only other element likely to be present in the mattes or concentrates that would interfere in the determination of cobalt. Aluminium is thought to interfere by absorbing some of the radiation from the excited cobalt and thereby diminishing the total cobalt radiation. This effect, however, is not particularly marked at concentrations of aluminium below about 500 p.p.m. in the final solution.[1] The addition of *iso*propyl alcohol appeared to decrease the adverse effect of aluminium and to increase the luminescence of cobalt. Application of the (L — H) method of measurement therefore served to give accurate results in the presence both aluminium and magnesium.

As only small amounts of potassium occurred in the concentrates and mattes investigated, no interference was experienced from this element. The copper line was unaffected by any of the above-mentioned elements. It was also observed that, if the sample contained nickel in concentrations above 0·5 per cent., this element could be determined at 361·9 mμ; slight interference from copper was noted.

An oxygen - acetylene flame was used in all determinations; background readings were consequently high. In order to overcome this and to obtain steadier galvanometer readings, *iso*propyl alcohol was added to the samples. It was found that the addition of 10 per cent. of *iso*propyl alcohol markedly enhanced the emission of cobalt and copper, afforded better aspiration and markedly steadied the galvanometer. Emission from iron was satisfactory without addition of *iso*propyl alcohol.

PREPARATION OF CALIBRATION GRAPHS—

Calibration graphs were plotted from dilutions of the reference solutions described under "Reagents," p. 507, care being taken to maintain the acid and alcohol concentrations at the stated levels.

Graphs for iron and cobalt, for which the (L — H) technique was to be used in sample determinations, were plotted from net relative-luminosity values obtained by averaging the readings at the relevant emission peaks and subtracting the mean of background (flame *plus* solvent) readings at 386·7 mμ. To ensure reasonable accuracy, the mean of at least five readings at each wavelength was taken.

As the peaks for all three elements are sharply defined, it was found to be advisable to rotate the wavelength drum back and forth until maximum deflection of the galvanometer was obtained with the reference solutions. When maximum deflection had been attained, the solvent was immediately substituted, by means of the quick-change ring beneath the burner capillary, and then the sample was aspirated in turn. This process was repeated until sufficient agreement was reached between readings. The values obtained were plotted on metric graph paper, the scale being 1 mm to 1 p.p.m. of the element.

No self-absorption was noted for the cobalt line at 387·4 mμ, the graph being linear up to a concentration of 1500 p.p.m. Background readings at 386·7 mμ were of the order of 25 scale divisions, thus giving 75 usable divisions, *i.e.*, 20 p.p.m. of cobalt per scale division. Readings were duplicated to 0·25 scale division (5 p.p.m.).

Slight self-absorption was observed for the iron line at 386·0 mμ up to a concentration of 600 p.p.m. Background readings at 386·7 mμ were of the order of 45 scale divisions, thus giving 11 p.p.m. of iron per usable scale division, *i.e.*, 3 p.p.m. per 0·25 scale division.

There was considerable self-absorption for the copper line at 324·8 mμ at concentrations greater than 250 p.p.m.; readings above this limit were unreliable. The best portion of the graph was that between 0 and 150 p.p.m., equivalent to 0 to 15 per cent. of copper. As mattes and concentrates rarely contain more than 15 per cent. of copper, this covered the expected range. Background readings at 324·8 mμ were of the order of 27 scale divisions, thus giving about 3·5 p.p.m. of copper per usable scale division, *i.e.*, 0·8 p.p.m. per 0·25 scale division.

METHOD

APPARATUS—

A Zeiss PMQ11 quartz spectrophotometer with flame attachment was used. An all-metal burner was used at an acetylene pressure of 130 mm (water gauge). Oxygen pressures of 0·30 kg per sq. cm in determining iron and 0·26 kg per sq. cm in determining cobalt and copper were used. Pressures were maintained by reduction valves on the fuel (5 lb per sq. inch) and oxygen (10 lb per sq. inch) cylinders and by micromanometers, fitted with sintered filters, in the secondary regulation panel supplied with the flame attachment. (These instrument settings are only a guide, as each instrument has its own characteristics.)

Maximum instrumental sensitivity, in conjunction with maximum response damping of the galvanometer (10-second response time), was used in determining iron and cobalt, with a 5-step reduction in sensitivity for copper.

A slit width of 0·025 mm, giving a band width of 0·40 mμ, was used in determining cobalt. Slit widths of 0·035 and 0·040 mm, giving band widths of 0·55 and 0·35 mμ, were used in determining iron and copper, respectively, thereby ensuring complete integration of the resonance lines and minimising interference effects.

REAGENTS—

All materials should be of analytical-reagent grade.

Hydrochloric acid, sp. gr. 1·18.

Nitric acid, sp. gr. 1·42.

Sulphuric acid, sp. gr. 1·84.

Ammonia solution, sp. gr. 0·880.

Hydrochloric acid, approximately 8 N—Dilute 70 ml of hydrochloric acid, sp. gr. 1·18, to 100 ml with water.

Hydrogen peroxide - sulphuric acid mixture—Add 6 ml of 100-volume hydrogen peroxide to 3 ml of sulphuric acid, sp. gr. 1·84, and cool.

Ethyl methyl ketone - chloroform mixture (2 + 1).

EDTA solution, 0·05 M—Dissolve 1·8605 g of the disodium salt of ethylenediaminetetra-acetic acid in 100 ml of water.

iso*Propyl alcohol.*

Bromine.

Cobalt reference solution—Dissolve 0·6 g of cobalt chloride, $CoCl_2.6H_2O$, in a mixture of 90 ml of 1 per cent. v/v hydrochloric acid and 10 ml of *iso*propyl alcohol. Make a 10-ml portion of this solution approximately *N* in ammonium hydroxide, and titrate against 0·05 *M* EDTA solution with murexide as indicator (1 ml of EDTA solution is equivalent to 2·947 mg of cobalt). Dilute the remainder of the solution with a (9 + 1) mixture of 1 per cent. v/v hydrochloric acid and *iso*propyl alcohol until it contains 1500 p.p.m. of cobalt.

Copper reference solution—Dissolve 0·0676 g of cupric chloride, $CuCl_2.2H_2O$, in a mixture of 90 ml of 1 per cent. v/v hydrochloric acid and 10 ml of *iso*propyl alcohol. This solution contains 250 p.p.m. of copper.

Iron reference solution—Dissolve 0·5 g of ferrous sulphate, $FeSO_4.7H_2O$, in 10 ml of hydrochloric acid, sp. gr. 1·18, and add 50 ml of water and 2 ml each of sulphuric acid, sp. gr. 1·84, and orthophosphoric acid, sp. gr. 1·75. Titrate against 0·1 *N* potassium dichromate with barium diphenylamine sulphonate as indicator, and calculate the weight of ferrous sulphate needed to prepare 100 ml of a solution containing 600 p.p.m. of iron. Dissolve this weight of ferrous sulphate in 100 ml of 3 per cent. v/v sulphuric acid.

PROCEDURE—

Weigh 1·0 g of sample into a 250-ml conical beaker, add 10 ml of hydrochloric acid, sp. gr. 1·18, and warm slightly to remove liberated hydrogen sulphide (from mattes). Add 2 ml of bromine to oxidise residual sulphur, and then add 5 ml of nitric acid, sp. gr. 1·42. Evaporate to dryness, add 2 ml of hydrochloric acid, sp. gr. 1·18, and again evaporate to dryness. Dissolve the residue in the minimum amount of 8 *N* hydrochloric acid, and filter the solution through a cotton-wool plug into a 250-ml separating funnel. Rinse the beaker with a minimum of 8 *N* hydrochloric acid, and pour the rinsings through the cotton-wool plug. Discard the plug and any insoluble matter.

Extract the solution with successive portions of ethyl methyl ketone - chloroform mixture (2 + 1), and combine the extracts in a second separating funnel. Finally, extract with a

10-ml portion of chloroform. Shake the combined extracts with 15 ml of 8 *N* hydrochloric acid, and run the organic layer into a clean 250-ml beaker. Evaporate the solvent, and remove the last few millilitres by means of a current of air. To the residue add cautiously, a little at a time, 9 ml of hydrogen peroxide - sulphuric acid mixture.[7] When the carbon has been destroyed, heat until fumes of sulphur trioxide appear (add more hydrogen peroxide, if necessary, until all carbon has been removed). Cool somewhat, dissolve in water, and boil until dissolution is complete. Cool, dilute to 100·0 ml with water, and then dilute a 10·0-ml portion of this solution to 100·0 ml with water. Use this solution for determining iron.

Combine the aqueous layers from the two separating funnels in a clean 250-ml beaker, and heat to remove residual solvent. Cautiously add 5 ml of nitric acid, sp. gr. 1·42, and evaporate to about 5 ml. Cool, dilute to about 50 ml with water, add 10 ml of *iso*propyl alcohol, and dilute to 100·0 ml with water. To a 10·0-ml portion of this solution add 9·0 ml of *iso*propyl alcohol, and dilute to 100·0 ml with water. Use these solutions for determining cobalt and copper, respectively.

Discussion of Results

Synthetic samples were prepared from pure salts to cover the full range of concentrations to be expected in practice. These samples were analysed by the proposed method; results were completely satisfactory. Interfering elements were then added, with the results described under "Interference," p. 505.

Determinations were then carried out on samples from various sources, and the results are shown in Table I. It can be seen that there is reasonable agreement between results by

Table I

Comparison between proposed and chemical methods

Sample No.	Method	Copper found, %	Iron found, %	Cobalt found, %
Cobalt matte—				
1	Flame photometry	14·0, 14·0	46·3, 46·5	8·5, 8·4
	Ion exchange	—	46·2, 46·1	8·37
	Electrolysis	13·96, 13·97	—	8·43
Cobalt concentrates—				
2	Flame photometry	0·86, 0·87	35·7, 35·6	1·53, 1·56
	Ion exchange	—	35·61, 35·59	1·50
	Electrolysis	0·86, 0·86	—	1·52
3	Flame photometry	8·8, 8·8	9·6, 9·4	21·3,* 21·2*
	Ion exchange	—	9·40, 9·33	21·16
	Electrolysis	8·77, 8·79	—	21·20
4	Flame photometry	9·4, 9·4	11·0, 10·9	20·8,* 20·8*
	Ion exchange	—	10·87, 10·91	20·74
	Electrolysis	9·41, 9·46	—	20·65

* Final solution diluted (1 + 1) before determination.

chemical methods of analysis and those by the proposed method. The duplicate chemical analyses were performed by two separate methods for iron and cobalt; copper was determined by electrolysis. The duplicate flame-photometric analyses were carried out on separately weighed and treated samples.

The main advantage of the proposed method is its rapidity; a duplicate determination can be carried out in about 2 hours.

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An Indicator Tube for the Determination of Trichloroethylene in Air

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An indicator tube is described for the determination of trichloroethylene vapour in air. The air sample is drawn through two tubes, which are joined in series immediately before the test. The first tube contains a layer of silica gel impregnated with potassium permanganate and orthophosphoric acid; the second tube contains silica gel impregnated with *o*-tolidine hydrochloride and serves to measure chlorine liberated by the first tube.

A simple rubber-bulb hand pump is described for use with these tubes.

The sensitivity, precision, stability and simplicity of the tubes make them suitable for routine industrial hygiene air analysis where trichloroethylene is used.

TRICHLOROETHYLENE is widely used as a dry-cleaning and de-greasing agent, and an analytical method for the routine control of its vapour in the atmosphere is desirable to ensure that machinery and ventilation systems function properly. As establishments where such operations are performed are frequently not equipped for chemical analyses, some simple test is required that does not need a skilled analyst or laboratory facilities. An indicator-tube method, of the type now well established and widely used for the determination of carbon monoxide in air,[1,2] appeared to offer the best chance of providing an acceptable analytical procedure for trichloroethylene.

The oxidation of certain chlorinated hydrocarbons with acidified potassium permanganate to liberate chlorine is well known and suggests a simple and sensitive method for determining trichloroethylene in air. An attempt to utilise this reaction by bubbling an air sample successively through acidified permanganate and *o*-tolidine solutions has not been entirely successful, owing to the high blank values encountered, which probably arise from the higher oxides of manganese and from other volatile oxidising substances, such as ozone, that are liberated from acid permanganate and produce a yellow colour with *o*-tolidine similar to that produced by chlorine. Indicator tubes containing silica gel impregnated with *o*-tolidine have been described[3] for determining chlorine in air, but such a tube containing a pre-reactor layer of silica gel impregnated with acidified permanganate was not satisfactory, as substances diffusing from the permanganate layer caused a progressive orange stain to develop on the *o*-tolidine layer during storage. The problem of progressive deterioration of the tubes has now been solved by keeping the two impregnated silica gel layers in separate tubes, which are connected immediately before use. Such a compound tube does not develop a yellow stain when a large volume of clean air is drawn through it.

PREPARATION OF INDICATOR TUBES

PURIFICATION OF SILICA GEL—

The silica gel used in this investigation was obtained from Silica Gel Ltd., graded 50 to 60 mesh. To remove metallic and other impurities, the silica gel was boiled under reflux with nitric acid for 1 to 2 hours and then washed in a stream of boiling water until free from nitrate. The granules were dried in air and heated at 150° C for 6 hours and then at 240° C for a further 6 hours.

IMPREGNATION OF SILICA GEL—

Acidified permanganate—Mix 4 ml of a 40 per cent. w/v aqueous solution of analytical-reagent grade orthophosphoric acid, sp.gr., 1·74 to 1·75 at 20° C, with 10 ml of a 5 per cent. w/v aqueous solution of potassium permanganate. Shake 5 ml of this mixture with 25 g of silica gel in a stoppered flask until it is uniformly dispersed.

o-Tolidine—Grind 0·25 g of analytical-reagent grade *o*-tolidine and 5 ml of concentrated hydrochloric acid into a paste, wash into a 250-ml calibrated flask with a further 20 ml of concentrated hydrochloric acid, and dilute to the mark with water. Add 12·5 ml of this

solution to 50 g of purified silica gel in a stoppered flask, and shake vigorously until the granules flow freely. This impregnated silica gel should be allowed to age for 2 weeks before it is used.

PREPARATION AND FILLING OF INDICATOR TUBES—

Selection and cleaning of glass tubes—Soda-glass tubing is cut into 12-inch lengths, the internal diameter of each tube is measured at both ends by means of a gauge and those tubes of bore within the range 3·4 to 3·6 mm are selected. These tubes are cleaned by immersion in a solution of a detergent for several hours and then washed in a pipette-washer for several hours. Finally the tubes are rinsed with distilled water and dried in an oven overnight.

Cleaning of glass wick—The most convenient method of retaining the silica gel in an indicator tube was by using short lengths of glass wick. This may be obtained from Jones,

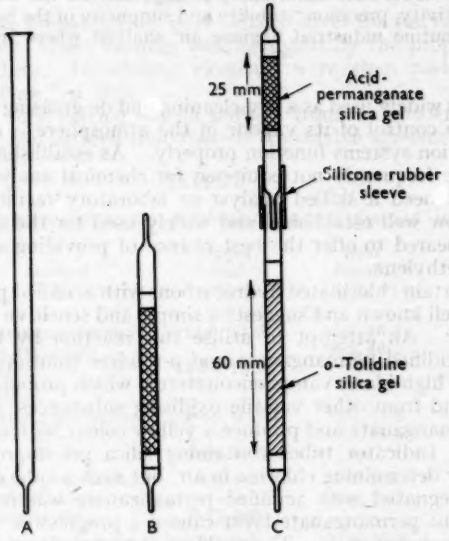

Fig. 1. Indicator tubes: A, tube before filling; B, double-sealed tube; C, compound acid permanganate and *o*-tolidine tube

Stroud & Co. Ltd., and the size suitable for the tubes described here is referred to by the makers as MC.3. The wick is cleaned by immersing it in a mixture of equal volumes of concentrated sulphuric and nitric acids and maintaining it for about 1½ hours at a temperature that causes a gentle evolution of nitric acid fumes. The wick is then washed in running tap-water for about 2 hours and rinsed several times in distilled water. A longer washing period is not necessary and may cause the wick to disintegrate. The wick is dried in an oven overnight and stored in a stoppered glass bottle.

Tube filling—The centre of one of the prepared lengths of glass tubing is drawn into a capillary, the tube is cut in half and the constricted ends are sealed. The open ends of the tubes are given a slight flange to assist filling (see Fig. 1 A). About 5 mm of clean dry glass wick is pushed down the tube with a clean dry glass rod and the required amount of granules is introduced by means of a suitable filling device.[2] The tube is tapped laterally until no further settling takes place, and then a second plug of glass wick is inserted and pushed down. The open end of the tube is then sealed to give a symmetrical form, as shown in Fig. 1 B.

For the acidified permanganate silica gel a final layer length of 25 mm is required. For the *o*-tolidine silica gel the required layer length is 60 mm, and the tube may either be sealed

at both ends, as described, or the open end can be cut shorter and connected to the double-sealed acidified permanganate tube by means of a silicone-rubber sleeve; a tube of this type is shown in Fig. 1 C. Silicone-rubber tubing was found to be somewhat superior to poly-(vinyl chloride) and much superior to rubber for this purpose; the use of these two last-named connections results in a progressive staining of the *o*-tolidine layer on long storage of the assembled tube. Just before use, the junction of the two tubes is bent to snap off the internal end of the acidified permanganate tube, which effects an air connection between the two layers, and to facilitate the breaking it is preferable to elongate the internal tapered end of the acidified permanganate tube. If separate double-sealed tubes are used, the ends of each are snapped off and the tubes joined together just before use by means of a piece of rubber tubing.

Performance of Indicator Tubes

Stability—

Experience with the *o*-tolidine tube for determining chlorine in air has shown that it is stable for at least 12 months. In the early stages of the development of the compound tube for determining trichloroethylene, an investigation was made into the effect of variation in the nature and concentration of the acid component of the acidified permanganate layer. Batches of silica gel were impregnated in the way described, but different concentrations of sulphuric, orthophosphoric and perchloric acids were used. Tubes were filled with the impregnated silica gels, sealed, attached to *o*-tolidine tubes and stored in the dark at room temperature. The tubes containing permanganate acidified with sulphuric and perchloric acids rapidly lost their purple colour and became brown; the colour of those acidified with orthophosphoric acid remained unchanged for at least 10 months. At monthly intervals, a pair of tubes was taken for a duplicate test in an atmosphere containing 130 p.p.m. of trichloroethylene, prepared by injecting the liquid at a known rate into a metered stream of air by means of a controlled fluid-feed atomiser.[4] After its ends had been broken off, the tube was attached to a rubber-bulb aspirator pump of the type described below, which gives a 60-ml sample of air, and provided with a capillary choke to restrict the filling time to about 100 seconds. When the test atmosphere was drawn through the tube, a deep orange stain having a bright yellow boundary developed on the *o*-tolidine layer; the extreme length of the stain was measured after three strokes of the pump. The results are shown in Table I, from which it is evident that the only formulation to give adequate stability is that containing 40 per cent. orthophosphoric acid, and this was used in all subsequent experiments.

Table I

Effect of Acid Component of Oxidising Layer on Stability

Each result is the mean of duplicate tests. The air sampled contained 130 p.p.m. of trichloroethylene

Acid	Acid concentration, %	Length of stain produced after oxidising layer had been prepared for— 0 weeks, mm	3 weeks, mm	7 weeks, mm	11 weeks, mm	16 weeks, mm	22 weeks, mm	35 weeks, mm	43 weeks, mm
Sulphuric	5	19·5	20	19	17	16	7	1	—
	10	20·5	20	14	8	4	—	—	—
	20	20·5	20	13·5	7	2	—	—	—
Orthophosphoric	10	12	14	19	16	18	16	11	—
	20	14	18	24·5	22	19·5	18·5	17	—
	40	20	25	27·5	26	25	26	23·5	20
Perchloric	2·5	16	9·5	5	—	—	—	—	—
	5	20·5	14	4·5	—	—	—	—	—
	10	24	14	2·5	—	—	—	—	—

Effect of Sampling Conditions—

When an air sample containing 130 p.p.m. of trichloroethylene was continuously drawn through an indicator tube at a constant rate of 60 ml per minute, by means of a water aspirator, there was a short interval before any stain developed. Thereafter, the relation of stain length

to sample volume was approximately linear, as shown in Fig. 2. At a sampling rate of 30 ml per minute, the curve was closely similar, but did not show the falling off at the highest concentration, which was observed at the higher sampling rate.

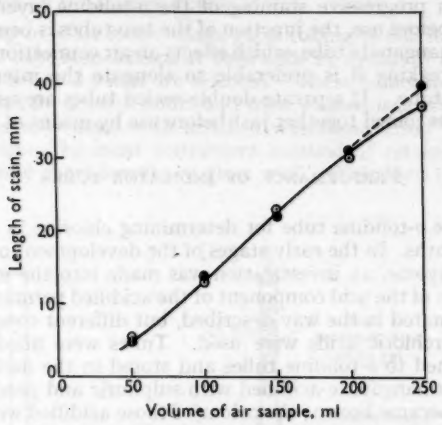

Fig. 2. Effect of sample volume and sampling rate on length of stain: ●, 30 ml per minute; ⊙, 60 ml per minute

The effect of the time lag between successive samples taken with a rubber-bulb pump has been studied. The pump gave a 60-ml air sample and was adjusted for a filling time of 60 seconds. The test atmosphere contained 130 p.p.m. of trichloroethylene, and the stain lengths obtained with successive strokes of the pump, and with an increasing interval between strokes, are shown in Table II. It can be seen that there is little difference in the stain length produced with intervals of 2 and 10 seconds between strokes, and in subsequent experiments a time interval of approximately 5 seconds was used.

TABLE II

EFFECT OF INTERVAL BETWEEN PUMP STROKES ON STAIN LENGTH

Each result is the mean of three tests. The air sampled contained 130 p.p.m. of trichloroethylene

Interval between strokes, seconds	Length of stain after— 1 stroke, mm	2 strokes, mm	3 strokes, mm	4 strokes, mm	5 strokes, mm
~ 2	8	20	31	40	50
10	8	19	30	40	50
60	9	25	35	52	—

CALIBRATION AND USE OF INDICATOR TUBES—

A batch of indicator tubes was prepared and measurements of the stain lengths were made at five different trichloroethylene concentrations, and with from 1 to 5 strokes of a rubber-bulb pump, three tubes being used for each determination. The sample volume for each stroke was 60 ml and the filling time was 60 seconds. The averages of these three measurements are shown in Fig. 3, the smooth curves in which were prepared and issued as a calibration chart for this batch of tubes, with the abscissae corresponding exactly to the stain length in millimetres. When the tubes were used to measure unknown trichloroethylene concentrations, from 1 to 4 pump strokes were made to produce, if possible, a stain about 20 mm long. The tube was then laid horizontally on the calibration chart with the beginning of the stain against the vertical concentration axis and was then moved up or down until the other end

of the stain coincided with the curve corresponding to the number of pump strokes made. The position of the tube on the concentration axis then indicated the concentration directly in parts per million of trichloroethylene.

The stain produced on the tube is orange and has a well defined bright yellow margin. The stain is stable for several hours, particularly if the tube is sealed. After 24 hours the colour has somewhat faded and the stain appears shorter, owing to the partial disappearance of the yellow margin. The assessment of an atmospheric concentration should therefore be made soon after the test is completed.

The reliability of the calibration chart depends on the use of a pump having characteristics similar to those of the pump used for the calibration. A rubber bulb provides the most convenient means of aspirating an air sample of known volume at a fairly constant rate;

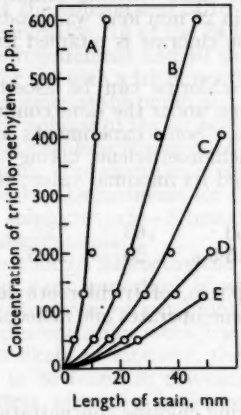

Fig. 3. Variation in length of stain with trichloroethylene concentration and number of pump strokes: curve A, 1 stroke; curve B, 2 strokes; curve C, 3 strokes; curve D, 4 strokes; curve E, 5 strokes

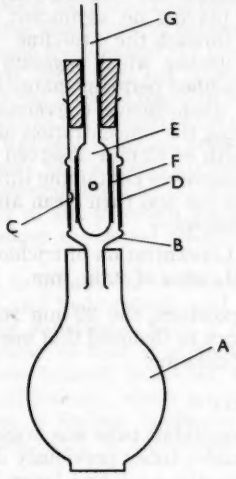

Fig. 4. Rubber-bulb pump: A, rubber bulb; B, glass tube; C, 2-mm hole; D and F, rubber sleeves; E, internal valve; G, connecting tube

the most suitable stroke volume is between 50 and 100 ml. In this investigation, a simple and inexpensive pump was constructed by attaching glass and latex-rubber sleeving valves to a rubber bulb of the type obtainable from Baird and Tatlock (London) Ltd. for use with pipettes. This bulb has a nominal capacity of 70 ml and its elasticity is sufficient to draw the air sample through the indicator tube at the required rate. A diagram of this pump assembly is shown in Fig. 4. An air sample of reproducible volume may be obtained by placing the bulb across the palm of the hand with the fingertips resting on the upper surface and then closing the hand sharply. The bulb is then allowed to re-assume its original shape and a few seconds later the next stroke is made. The average volume of air sampled by one stroke of the pump is in the region of 60 ml and the standard deviation of a volume measurement by an experienced operator is 0·5 ml.

PRECISION OF RESULTS—

The standard deviation from the mean of twelve repeated determinations of stain length performed by the same individual on an air sample containing 130 p.p.m. of trichloroethylene under the conditions detailed in Fig. 3 was as follows—

Number of strokes	1	2	3	4	5
Standard deviation of stain length, mm	0·83	1·4	1·7	1·7	1·6

NATURE OF THE CHEMICAL REACTION—

When air containing trichloroethylene was sampled through the indicator tube, there was a time lag before colour developed. If clean air was drawn through the tube after the sample had been taken, the stain length increased considerably. One stroke in an atmosphere containing 130 p.p.m. of trichloroethylene produced a stain 7 mm long, which was afterwards increased to 18 mm by taking 5 pump strokes of clean air through the tube. The inference is that the vapour is rapidly adsorbed on the acidified permanganate - silica gel layer and that chlorine is then either liberated by a slower reaction or is reversibly adsorbed on the gel to some extent. When an atmosphere containing 64 p.p.m. of chlorine was sampled through the complete tube with 2 pump strokes, a stain 22 mm long was produced and did not increase in length when clean air was subsequently drawn through the tube. This leads to the conclusion that the rate of evolution of chlorine from adsorbed trichloroethylene on the acidified permanganate - silica gel layer is controlled by the reaction rate, reversible adsorption of chlorine playing no significant part. However, when the same chlorine atmosphere was sampled through the *o*-tolidine - silica gel tube alone, a stain 26 mm long was produced with 2 pump strokes, which suggests that a small portion of the chlorine is retained irreversibly on the acidified permanganate - silica gel layer.

The quantitative conversion of trichloroethylene to chlorine can be ascertained by determining the concentration of trichloroethylene that gives, under the same conditions, the stain length of 22 mm observed with 64 p.p.m. of chlorine. Some experiments were made with atmospheres containing different concentrations of trichloroethylene, taking a 2 pump-stroke sample and then clean air until the stain had reached its maximal value; the results were as follows—

Concentration of trichloroethylene, p.p.m. ..	53	63	72
Length of stain, mm	15·5	20	23·5

By interpolation, the 22-mm stain was produced by 68 p.p.m. of trichloroethylene, from which it can be deduced that one molecule of trichloroethylene liberates one molecule, or two atoms, of chlorine.

SPECIFICITY—

The *o*-tolidine tube was originally developed for measuring chlorine concentrations in air and resembles tubes previously described for this purpose.[3] Chlorine, and substances that can oxidise the *o*-tolidine layer in a similar manner and pass intact through the acidified permanganate layer, will give a positive reaction. Yellow stains will also be obtained from substances that, like trichloroethylene, give rise to oxidising substances after permanganate oxidation; the only other halogenated hydrocarbon that has been found to behave in this way is perchloroethylene (tetrachloroethylene). Probably the most likely interfering substance of this nature to be encountered in a factory or laboratory atmosphere is hydrochloric acid vapour.

DISCUSSION OF RESULTS

The tests made have shown that the trichloroethylene indicator tubes have a precision adequate for industrial hygiene air analysis and that their life is in the region of 9 months, which should be sufficient to permit such tubes to be manufactured and distributed commercially. The tube containing acidified permanganate should retain its purple colour over this period, and any tube that turns brown should be regarded with suspicion. The initial increase in sensitivity with storage indicated in Table I needs confirmation, but it is desirable that each batch should be kept for a few weeks before it is calibrated. No extensive information is yet available on batch variation, but it is desirable that every batch made should be calibrated, a random sample being taken for each test concentration. The conditions of air sampling during calibration should be identical with those recommended in the instructions for use issued with the tubes.

Fig. 3 indicates a form of calibration chart that could be issued with each batch of indicator tubes and permits coverage of a wider range of concentrations. It should be noted that, if the *o*-tolidine tube has been packed unevenly, the margin of the stain may be irregular, and when the tube is applied to the chart to assess the concentration it must be rotated in order to estimate the average length of the stain. As the maximal allowable concentration of trichloroethylene recommended by most authorities is 200 p.p.m., the range

50 to 400 p.p.m. is the most important, and the graph shows that the calibration could be restricted to the curve for 3 pump strokes. If concentrations below 50 p.p.m. are of interest, the calibration graph should be made with more than 5 pump strokes. The assessment of the concentration would be facilitated if a scale corresponding to the stain lengths obtained with a stated number of pump strokes was attached to or inscribed on each tube.

If a test gives a negative result, the tube may be used again, provided that the acidified permanganate layer retains its purple colour. If a yellow stain is obtained in a test, the *o*-tolidine tube, if it is of the double-ended type, may be reversed and used again with the same acidified permanganate tube, provided that the latter does not show much brown discoloration and has been purged with clean air to remove any retained chlorine.

The validity of the calibration of the tubes depends on the existence of a pump having uniform characteristics. The rubber-bulb pump described is suitable for this purpose, provided that the bulbs are selected to conform to a specification; measurements of volume and filling time made on a manufacturer's delivery of 24 rubber bulbs suggested that limits of 57 to 59 ml for the volume and 21 to 26 seconds for the filling time would not be unreasonable. By this specification, 15 of the 24 bulbs conformed to the volume requirement, 17 conformed to the time requirement and 10 conformed to both. The inner valve does not appear to be necessary for use with a trichloroethylene indicator tube, but it has a useful function in reducing the dead space of the pump and thereby reducing the influence of the tension of the external valve on the volume of the air sample.[5] Although this pump has been designed primarily for use with the trichloroethylene and other indicator tubes, it may find a useful application in other methods. For example, it could be used in the method recommended by the Ministry of Labour Factory Department for determining benzene vapour in air, in which air is drawn through a sulphuric acid - formaldehyde reagent until the colour developed resembles that of a permanent standard.[6]

The test for trichloroethylene with these tubes is subject to interference from a few substances, the most important of which are perchloroethylene and hydrochloric acid vapour. With the exception of perchloroethylene, all the interfering substances have a maximal allowable concentration much less than that of trichloroethylene, so that, if present in concentrations likely to interfere, they give rise to a serious toxic hazard; moreover, they are not likely to be found in dry-cleaning and de-greasing establishments, which are the most useful outlets for these indicator tubes. Perchloroethylene is finding applications as a replacement for trichloroethylene, and, if required, the tubes could be calibrated for this vapour.

Technical assistance in this investigation was provided by Mr. T. V. H. Chalker.

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Notes

THE PHOTOMETRIC DETERMINATION OF FERRIC IRON BY CATECHOL

FAINTLY acid solutions containing less than 200 p.p.m. of ferric iron produce a violet colour with catechol. Bernouilli's method[1] was found to be unsuitable for determining iron in soil extracts, as the correct acidity was difficult to reproduce and aluminium interfered. Ferric iron can be determined consistently and accurately by the method described below.

METHOD

REAGENTS—

Buffer solution, pH 5·3—Mix 975 ml of *M*/15 potassium dihydrogen orthophosphate and 25 ml of *M*/15 disodium hydrogen orthophosphate.

Sodium hydroxide solution, 8 *per cent. w/v.*

Catechol solution, 2 *per cent. w/v.*

p-*Nitrophenol solution*, 0·2 *per cent. w/v.*

PROCEDURE—

By pipette, place a sample containing up to 1·5 mg of iron in acid solution in a 100-ml calibrated flask, and add about 50 ml of water. With *p*-nitrophenol as indicator, neutralise the solution by adding 8 per cent. w/v sodium hydroxide solution until the colour changes to yellow, and then add 2 drops more. Add 20 ml of 2 per cent. w/v catechol solution, and set aside for 15 minutes. (The catechol solution produces a cherry-red colour under these conditions; if the colour is tinged with blue, add a further 1 drop of sodium hydroxide solution.) Add 10 ml of buffer solution, dilute to the mark immediately, and set aside for 1 hour. Measure the optical density of the solution at 580 mμ.

RESULTS

It was found that Beer's law was obeyed for concentrations of iron between 0 and 15 p.p.m.

The accuracy of the method was tested by measuring the optical densities of a series of solutions containing different concentrations of iron in the presence of 5 p.p.m. of aluminium and 0·4 p.p.m. each of copper, nickel, cobalt, manganese and tungsten. Vanadium was found to interfere strongly, even in low concentrations, and iron could not be determined in its presence.

The recovery of iron from a diluted digest of soil was measured. A 2-ml portion of the soil solution, containing approximately 100 μg of iron per ml, was placed, by pipette in a 100-ml calibrated flask, and water was added. Standard iron solution was then added and colour was developed in the usual way.

The results are shown in Table I.

TABLE I

RESULTS FOR VARIOUS SOLUTIONS CONTAINING IRON

Concentration of iron present, μg per ml	Mean optical density per μg of iron of— standard iron solution	standard iron solution *plus* other ions	solution of soil digest
2	0·0625	0·0640	0·0605
4	0·0616	0·0637	0·0622
5	0·0614	0·0636	0·0620
7	0·0614	0·0627	0·0616
9	0·0617	0·0618	0·0622
10	0·0615	0·0618	0·0620
15	0·0611	0·0610	0·0613

I thank the Director and Governing Body of the Tea Research Institute for permission to publish this Note.

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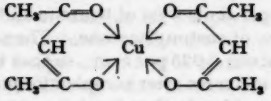
SPECTROPHOTOMETRIC DETERMINATION OF ACETYLACETONE WITH CUPRIC ACETATE

METHODS described for the determination of acetylacetone include saponification, potentiometric titration with standard alkali[1] and a spectrophotometric method in which ferric iron is used.[2] These methods are not suitable for determining acetylacetone in mixtures containing impurities of esters or organic acids, and the method involving ferric iron cannot be applied to highly coloured solutions.

Acetylacetone, like other β-diketones, reacts with cupric acetate solution under specific conditions of pH to form a blue chelate derivative, which is sparingly soluble in water; the derivative has the following formula—



This reaction is the basis of a method in which acetylacetone is allowed to react with an excess of cupric acetate reagent solution and the excess of copper is determined iodimetrically.[3] This method cannot be used in the presence of unsaturated materials and other compounds liable to react with iodine, but the copper acetylacetonate can be extracted by chloroform to give a blue solution, in which acetylacetone can be determined spectrophotometrically.

EXPERIMENTAL

ABSORPTION SPECTRUM—

All optical measurements were made in 1-cm glass cells with a Hilger Uvispek spectrophotometer. Fig. 1 shows the absorption spectrum of a 0·5 per cent. w/v solution of copper acetylacetonate in chloroform. It exhibits an absorption band having a maximum at 650 mμ, which is sufficiently broad not to make the wavelength setting highly critical. It has been found that, at

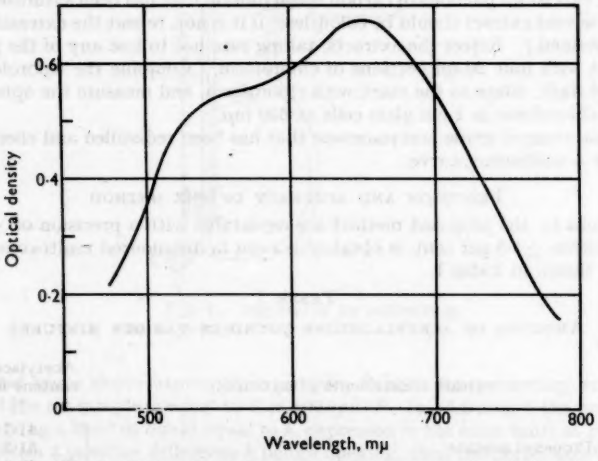


Fig. 1 Absorption spectrum of 0·5 per cent. w/v solution of copper acetylacetonate in chloroform measured in 1-cm glass cells against chloroform.

650 mμ, solutions of the complex obey Beer's law over a concentration range equivalent to 0 to 600 mg of acetylacetone per 100 ml of chloroform and have optical densities of up to about 1·0 in a 1-cm cell. The proposed method was calibrated by using a sample of analytical-reagent grade acetylacetone (obtained from the British Drug Houses Ltd.), which, after it had been redistilled twice, gave an analysis of 100·1 per cent. by saponification and showed no impurity when examined by vapour-phase chromatography. The coloured chloroform solution is stable; measurements made after it had been set aside for 24 hours were identical with those made immediately after preparation.

EFFECT OF pH—

The optimum pH for the quantitative formation of copper acetylacetonate is 5·2 to 6·0.[3] This is maintained by carrying out the reaction in sodium acetate buffer solution. With this buffer, acetylacetone has been quantitatively determined in 1-g samples containing up to 20 per cent. of acetic acid. It is recommended that samples more acid than this be neutralised with sodium hydroxide before the determination.

EFFECT OF ORGANIC IMPURITIES—

The method has been tested in the presence of mixtures of compounds normally encountered in impure samples of acetylacetone. Results were satisfactory in the presence of up to 50 per cent. w/w of *iso*propenyl acetate, up to 20 per cent. w/w of acetic acid and acetic anhydride, up to 50 per cent. w/w of acetone, up to 10 per cent. w/w of benzene and toluene, up to 10 per cent. w/w of diacetyl and up to 50 per cent. w/w of acetonylacetone. The solubility of copper acetylacetonate in carbon tetrachloride at 20° C is about 0·025 per cent., so that tars and discoloured organic matter can be conveniently removed from mixtures after complex formation and before chloroform extraction by extraction with carbon tetrachloride that has been saturated with the complex.

METHOD

REAGENTS—

Cupric acetate solution—Dissolve 50 g of analytical-reagent grade cupric acetate monohydrate in 1 litre of water, and filter the solution.

Sodium acetate buffer solution—Dissolve 200 g of sodium acetate trihydrate in 1 litre of water.

PROCEDURE—

Measure 25 ml each of cupric acetate solution and sodium acetate buffer solution into a 250-ml stoppered glass flask, and weigh into it 0·5 to 1·2 ml of sample (expected to contain 300 to 500 mg of acetylacetone). Insert the stopper, and shake the flask frequently over a period of 5 minutes. By means of a filter funnel, transfer the mixture quantitatively to a 250-ml separating funnel, and extract with two 20-ml portions of carbon tetrachloride that has been saturated with the copper complex. (The second extract should be colourless; if it is not, repeat the extraction until a colourless extract is obtained.) Reject the extracts, taking care not to lose any of the precipitated complex, and extract with four 20-ml portions of chloroform. Combine the chloroform extracts in a 100-ml calibrated flask, dilute to the mark with chloroform, and measure the optical density of the solution against chloroform in 1-cm glass cells at 650 mμ.

Use analytical-reagent grade acetylacetone that has been redistilled and checked for purity to obtain values for a calibration curve.

PRECISION AND ACCURACY OF THE METHOD

Determinations by the proposed method are repeatable with a precision of ±1 per cent., and an accuracy to within ±1·5 per cent. is obtainable even in discoloured multi-component mixtures. Some results are shown in Table I.

TABLE I

AMOUNTS OF ACETYLACETONE FOUND IN VARIOUS MIXTURES

Theoretical acetylacetone content, %	Other constituents of mixture	Acetylacetone content found, %	Error, %
41·3	*iso*Propenyl acetate	41·7	+0·96
51·9	*iso*Propenyl acetate	51·3	−1·13
60·2	*iso*Propenyl acetate	60·6	+0·66
89·9	Diacetyl	89·5	−0·45
49·1	Acetonylacetone	49·0	−0·2
90·2	Acetic anhydride	90·15	−0·055
90·7	Acetone	91·3	+0·22
92·0	Toluene	92·1	+0·11
27·2	Acetone and acetic acid (50%), acetic anhydride and tarry matter	26·8	−1·46
54·5	Acetic acid, acetic anhydride, acetone, *iso*propenyl acetate, toluene and tarry matter	54·2	−0·55

I thank the Directors of Courtaulds Limited for permission to publish this Note.

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COURTAULDS LTD.
COVENTRY

R. J. STARKEY

Received *February 9th*, 1959

THE CALIBRATION OF HAND PUMPS FOR AIR SAMPLING

WHEN a hand pump is used to take an air sample for the purpose of industrial hygiene or other air analysis, it is necessary to know the volume of the air sample at atmospheric pressure. This volume will depend mainly on the swept volume of a piston pump, or on the deformation of a rubber-bulb pump at compression, but also on other factors, such as the efficiency of closure of the valves. The dead space in the pump may also influence the volume of the air sample if the elastic nature of the air-exit valve during compression permits the development of a significant pressure in the dead space; if the swept volume of the pump is V and the dead space v, and p is the excess

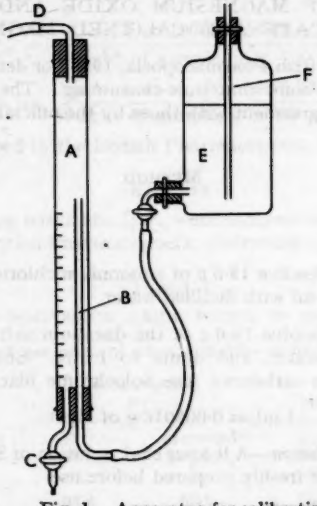

Fig. 1. Apparatus for calibrating hand pumps

pressure in the dead space above atmospheric pressure P, then the percentage error in assuming that the volume of the air sample is equal to V is $100\,vp/VP$. In addition, if the pump is connected to a bubbler containing a head of liquid equal to h, expressed in the same units as p and P, or if the air-inlet valve requires a pressure difference h before opening, then the percentage error due to this is $100\,h/P$; the total possible error is therefore $100(vp + hV)/VP$. With ageing of the pump, the magnitude of this error may alter, owing to a change in the elasticity of the valve.

The apparatus shown in Fig. 1, which may be constructed from ordinary laboratory glassware, has been used in this laboratory for several years to check the efficiency of hand pumps, as it gives a direct reading of the volume of the air sample at atmospheric pressure taken under actual conditions of use. For measuring air volumes of about 120 ml, the glass tube, A, should be about 40 cm long and 3 cm in diameter. Its lower end is fitted with a rubber stopper through which passes a glass tube, B, rising to a height of about 25 cm within A, and a drain cock, C. The lower end of tube B is connected by means of rubber tubing to the outlet of a water aspirator, E, the neck of which is closed by a stopper fitted with a water-levelling tube, F. The pump to be tested is connected by means of rubber tubing to a glass tube, D, which passes through a rubber stopper in

the upper end of tube A. If the pump is to be used with a liquid bubbler, it is preferable to connect it to the apparatus through the bubbler, charged with an appropriate amount of the liquid.

In operation, the stopcock of the aspirator is opened and water is allowed to flow into B with D open to the atmosphere. The relative heights of the aspirator and of tube B are then adjusted so that the water level is just at the top of B, but does not overflow. Stopcock C is opened to drain tube A, and then closed. The pump to be tested is attached at D and operated at the required sampling rate. Water from the aspirator enters A to replace the air withdrawn by the pump, and the pressure in A does not depart appreciably from atmospheric pressure unless the pumping rate is extremely fast.

The volume of water in A gives a measure of the volume of air sampled by the pump at atmospheric pressure; this volume may be determined by draining off the water into a graduated cylinder. Alternatively, tube A may be calibrated to give a direct reading of the volume.

IMPERIAL CHEMICAL INDUSTRIES LIMITED J. C. GAGE
INDUSTRIAL HYGIENE RESEARCH LABORATORIES
THE FRYTHE, WELWYN, HERTS.

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THE DETERMINATION OF MAGNESIUM OXIDE AND SILICA IN MAGNESIUM TRISILICATE AND CALCINED MAGNESITE

THE method described in the British Pharmacopoeia, 1958, for determining magnesium oxide and silica in magnesium trisilicate is somewhat time-consuming. The method described here is more rapid and gives results in good agreement with those by the official assay procedure.

METHOD

REAGENTS—

Perchloric acid, 60 *per cent.*

Ammonia buffer solution—Dissolve 13·5 g of ammonium chloride in 130 ml of strong ammonia solution, B.P., and dilute to 200 ml with distilled water.

EDTA solution, 0·05 M—Dissolve 18·6 g of the disodium salt of ethylenediaminetetra-acetic acid, $C_{10}H_{14}O_8N_2Na_2.2H_2O$, in water, and dilute to 1 litre. Standardise this solution against analytical-reagent grade calcium carbonate (use Solochrome black indicator solution).

$$1 \text{ ml} \equiv 0{\cdot}002016 \text{ g of MgO}$$

Solochrome black indicator solution—A 0·5 per cent. solution of Solochrome black in 95 per cent. ethanol. This solution should be freshly prepared before use.

Hydrofluoric acid, 40 *per cent. w/v.*

Sulphuric acid, *sp. gr.*, 1·84.

PROCEDURE—

To about 0·5 g of sample in a 150-ml beaker add 5 ml of water and 10 ml of 60 per cent. perchloric acid, and heat on a hot-plate until dense white fumes are evolved. Cover the beaker with a watch-glass, and heat for a further 3 hours. Allow to cool, and dilute with about 30 ml of water. Filter the solution, and collect the filtrate in a 250-ml calibrated flask. Wash the beaker and filter-paper with hot water, and collect the washings in the flask. (It is important to wash the filter-paper free of perchloric acid, and about 200 ml of hot water should be used for this purpose.) Allow the contents of the flask to cool, and dilute to the mark.

Determination of silica—Treat the residue on the filter-paper by the procedure described in the British Pharmacopoeia, 1958, beginning at "Dry and ignite the filter-paper. . . ."

Determination of magnesium oxide—To a 100-ml aliquot of the filtrate in a conical flask add 10 ml of ammonia buffer solution and a few drops of Solochrome black indicator solution, and titrate to a pure blue colour with 0·05 *M* EDTA solution.

Application to the analysis of calcined magnesite

Reagents—

Calcon indicator solution—Dissolve 0·2 g of Solochrome dark blue (obtained from the British Drug Houses Ltd.) in 50 ml of industrial methylated spirit.

Sodium hydroxide, N.

Diethylamine—Technical grade.

Procedure—

To about 2 g of sample in a 150-ml beaker add 20 ml of 60 per cent. perchloric acid and 10 ml of water. Treat as for magnesium trisilicate, but only heat for a further 45 minutes after the evolution of white fumes. Dilute the filtrate to 1000 ml in a calibrated flask. Determine the total magnesium and calcium in a 25-ml aliquot as described above. (Let this titration be a ml of 0·05 M EDTA solution.)

To determine the calcium, neutralise a 100-ml aliquot of the filtrate to litmus paper with N sodium hydroxide. Add 15 ml of diethylamine, 50 ml of water and 6 drops of calcon indicator solution. Titrate to a blue colour with 0·05 M EDTA solution. (Let this titration be b ml of EDTA solution.)

Calculate the amounts of calcium and magnesium oxides in the sample by using the following expressions—

$$\text{CaO present, \%} = \frac{b \times 1000 \times 56{\cdot}08 \times 100}{\text{Weight of sample, g} \times 100 \times 20{,}000}$$

$$\text{MgO present, \%} = \frac{(a - b/4) \times 1000 \times 40{\cdot}32 \times 100}{\text{Weight of sample, g} \times 25 \times 20{,}000}$$

Determine silica as described in the British Pharmacopoeia, 1958.

Results

Some samples of magnesium trisilicate, B.P., were analysed by the proposed procedure and by the method described in the British Pharmacopoeia; the results are shown in Table I.

Table I

Amounts of silica and magnesium oxide found in magnesium trisilicate B.P.

The official limits are 66·0 to 69·5 per cent. of silica and 30·0 to 32·5 per cent. of magnesium oxide

	Sample No.	Silica found by— B.P. method, %	Silica found by— proposed method, %	Magnesium oxide found by— B.P. method, %	Magnesium oxide found by— proposed method, %
Heavy	1	68·4	68·9	31·4	31·5
	2	65·3	65·1, 64·9	29·5	30·2, 30·3
	3	66·1, 65·7	65·9, 66·3	29·5, 29·3	29·4, 29·2
	4	68·4	68·8	31·6	31·5
	5	—	68·3	—	30·0
Light	1	69·3, 69·4	69·4, 69·9	30·3, 30·8	31·0, 31·1
	2	69·4	69·4	30·8	31·0
	3	—	68·1	—	31·3
	4	—	67·7	—	30·9
	5	65·5	65·6	30·8	30·4

Three samples of calcined magnesite were also analysed by the proposed procedure, with the following results—

Sample No.	1	2	3
Silica found, %	3·23	3·17, 3·16	3·73, 3·56
Magnesium oxide found, %	85·0	89·0, 89·1	88·1, 88·1
Calcium oxide found, %	1·4	1·8, 1·8	1·7, 1·7

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Received *March 18th*, 1959

A METHOD FOR DETERMINING POTASSIUM GUAIACOLSULPHONATE IN PHARMACEUTICAL PREPARATIONS

No method has so far been described for the determination of potassium guaiacolsulphonate in pharmaceutical preparations. The British Pharmaceutical Codex, 1949, monograph on the drug does not include an assay, and the U.S. National Formulary describes an assay based on conversion to sulphate, which, however, is not applicable to proprietary combinations.

Numerous methods are available for oxidising organic sulphur to sulphate. Miko[1] has used hydrochloric acid and hydrogen peroxide to oxidise sulphonamides, and Koszegi and Barcsay[2] have used a mixture of potassium dichromate and orthophosphoric acid. Milton, Hoskins and Jackman[3] have described a method in which the material is oxidised with a mixture of nitric acid and ammonium nitrate. These three oxidation procedures were studied, with slight variations, and it was found that Milton, Hoskins and Jackman's method could be used for the quantitative conversion of potassium guaiacolsulphonate in syrups to sulphate.

Proprietary cough syrups containing potassium guaiacolsulphonate and other antitussive drugs were studied, the sulphur being oxidised to sulphate and determined gravimetrically. In addition, known amounts of potassium guaiacolsulphonate were added to aliquots of the samples and the recovery of the added salt was determined in each instance. The purity of the potassium guaiacolsulphonate was determined by the method described in the U.S. National Formulary.

Miko's method[1] was tedious and gave results that were 2 per cent. low. A variation of Koszegi and Barcsay's method,[2] in which potassium permanganate and orthophosphoric acid were used, gave fairly accurate results, but the precipitate of barium sulphate appeared to carry down impurities. Milton, Hoskins and Jackman's method[3] does not introduce any interfering ions and was found to be simple, rapid and accurate.

Method

Procedure—

Transfer an aliquot of the sample containing about 50 mg of potassium guaiacolsulphonate to a 300-ml Kjeldahl flask, and add 10 ml of concentrated nitric acid. Cautiously warm the flask over a small flame until effervescence ceases. Add 10 ml of the oxidising reagent solution (a 50 per cent. w/v solution of ammonium nitrate in 25 per cent. nitric acid), and heat gently until the volume is considerably reduced, taking care to avoid charring. Add more of the oxidising reagent at intervals, and continue to boil. (The colour of the mixture changes from brown to yellow and finally disappears.) When the oxidation is complete, as indicated by a clear colourless melt, heat more strongly to volatilise the excess of ammonium nitrate (hold the flask over a naked flame to expel the salt that sublimes on its sides). Add 2 ml of concentrated hydrochloric acid, evaporate to dryness, and heat to remove all nitric acid. Dissolve the residue in 15 ml of *N* hydrochloric acid, and evaporate the solution to half this volume. Transfer the solution to a 150-ml beaker by using 50 ml of water, boil, and add 5 ml of a 5 per cent. w/v solution of barium chloride dropwise to precipitate sulphate. Collect the precipitate on a weighed No. 4 sintered-glass crucible, and wash it four times with water, six times with 5-ml portions of rectified spirit and then six times with 5-ml portions of diethyl ether. Dry by suction, place in a vacuum desiccator for 30 minutes, and weigh (1 mg of barium sulphate is equivalent to 1·038 mg of potassium guaiacolsulphonate).

When applied to the salt alone, the proposed method gave results identical with those obtained by the procedure described in the U.S. National Formulary. The recovery of added potassium guaiacolsulphonate from syrups was 100 per cent.

We thank the Director, King Institute, Guindy, and the Government Analyst, Madras, for facilities given to us to carry out this study.

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Ministry of Agriculture, Fisheries and Food

STATUTORY INSTRUMENT*

1959—No. 1098. **The Condensed Milk Regulations, 1959.** Price 4d.

These Regulations, which came into operation on June 26th, 1959, re-enact in consolidated and revised form the Public Health (Condensed Milk) Regulations, 1923, as subsequently amended. They also provide for the sale of half cream sweetened and unsweetened condensed milk and prescribe standards accordingly.

Book Reviews

THE CHEMICAL ANALYSIS OF FOOD AND FOOD PRODUCTS. By MORRIS B. JACOBS, Ph.D. Third Edition. Pp. xxiv + 970. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Co. Inc. 1958. Price $13.75; 103s. 6d.

This edition differs from the second edition, which appeared in 1951, only in the terminal addition of three new chapters; the first twenty-one chapters retain precisely the pagination and the misprints of the previous edition. The three new chapters deal with radiochemical determinations, pesticide residues and artificial sweetening agents.

The preface to the first edition stated that the book was designed for use as an educational text and as a manual for manufacturers for control work. Both the student and the analyst in a food-control laboratory would find much useful information in the book, but they, and chemists in what the author calls "regulatory laboratories," would look in vain for guidance and instructions on a number of matters that they might well expect to obtain from it. A student, and indeed a control chemist called upon to assess the quality of a food not previously examined, needs guidance on the tests he should select for his scheme of analysis and in particular on the interpretation to be placed on the results he obtains. The book is not very helpful in these directions and indeed may be misleading. This defect is perhaps scarcely avoidable when a practical manual with such a wide coverage is the work of a single author.

This book will be mainly useful as a source of details of a method or methods that could be employed for the detection or determination of a specific substance. A. J. AMOS

ADVANCED ANALYTICAL CHEMISTRY. By LOUIS MEITES and HENRY C. THOMAS, with a chapter on The Absorption of Infrared Radiation by ROBERT P. BAUMAN. Pp. xii + 540. New York, Toronto and London: McGraw-Hill Book Co. Inc. 1958. Price $8.90; 69s.

This book, which is written jointly by the professors of analytical chemistry at Brooklyn Polytechnic Institute and the University of North Carolina, is a departure in several respects from normal run-of-the-mill text-books on analytical chemistry produced so prolifically in the U.S.A. It is, superficially at least, a book on a selected range of instrumental methods of inorganic analysis; these are potentiometry (oxidation - reduction and acid - base), conductometry, polarography, electrolytic methods (including coulometry), spectrophotometry (ultra-violet, visible and infra-red), radiochemical methods, ion exchange and chromatography. The first chapter discourses briefly on the nature of analytical chemistry and is followed by one on ionic equilibria in solution, which places fairly and squarely before the student the difficulties facing the analytical chemist in applying the fundamental laws of chemistry to his somewhat complex problems. The case for and against the adoption of the active mass, molar concentration or formal concentration method is well argued. The final chapter deals with approximately ninety laboratory experiments based on the above-mentioned techniques.

The subject matter is cohesive, *i.e.*, chapters are not sealed off as isolated monographs; the inter-relationships are well traced and the merits and de-merits of one analytical method relative to another are quite prominently featured. This treatment is most valuable for student instruction. The way in which the authors have consistently placed emphasis on the fundamental physico-chemical basis of analytical chemistry is to my mind refreshing and somewhat unusual in a book of this type, which too often deal with instrumental methodology. The characteristic series of numerical exercises common to most American texts appears at the end of each chapter. However, one sometimes has the feeling that these belong more appropriately to a course on physical chemistry. The final chapter on the development of an analytical method is well and simply written and is worthy of the space it occupies. The section on ultra-violet absorption is exceptionally good for student use. In my opinion this book is vastly superior to the average text-book on instrumental methods of analysis. T. S. WEST

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

Publications Received

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY. Complete Translation. Executive Editor of English Edition: Professor P. L. ROBINSON, D.Sc., F.R.I.C. Volume 4, Number 1, January, 1959. Pp. vi + 105. London: The Chemical Society. Distributors: Cleaver-Hume Press Ltd., London. Annual Subscription Rates: Ordinary, £30; $90.00: Libraries of Universities and Technical Colleges, £22 10s.; $67.50. Single Copies: £4; $12.00.

This translation will appear in monthly parts corresponding to those of the Russian original. The publication is supported by the Department of Scientific and Industrial Research, and the translations are supplied by Infosearch Ltd., London.

AROMATIC SUBSTITUTION: NITRATION AND HALOGENATION. By P. B. D. DE LA MARE, M.Sc., D.Sc., and J. H. RIDD, B.Sc., Ph.D. Pp. viii + 252. London: Butterworths Scientific Publications; New York: Academic Press Inc. 1959. Price 50s.; $9.00.

BRITISH PHARMACOPOEIA 1958: AMENDMENTS, September, 1958, and June, 1959. Pp. 7. London: The Pharmaceutical Press for The General Medical Council. 1959. Gratis.

Copies of this leaflet may be obtained on application, enclosing a stamped addressed envelope, from The Secretary, British Pharmacopoeia Commission, General Medical Council Office, 44 Hallam Street, London, W.1.

ELECTROPHORESIS: THEORY, METHODS AND APPLICATIONS. Edited by MILAN BIER. Pp. xx + 563. New York and London: Academic Press Inc. 1959. Price $15.00; 107s. 6d.

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COMPREHENSIVE ANALYTICAL CHEMISTRY. Volume IA. CLASSICAL ANALYSIS. Edited by CECIL L. WILSON, Ph.D., D.Sc., F.R.I.C., F.I.C.I, and DAVID W. WILSON, M.Sc., F.R.I.C. Pp. xx + 577. Amsterdam, London, New York and Princeton: Elsevier Publishing Co.; London: D. Van Nostrand Co. Ltd. 1959. Price 105s.

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INDUSTRIAL FATTY ACIDS AND THEIR APPLICATIONS. Edited by E. SCOTT PATTISON. Pp. vi + 230. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1959. Price $7.00; 56s.

SILICONES. By R. N. MEALS and F. M. LEWIS. Pp. xii + 267. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1959. Price $6.00; 48s.

ENCYCLOPEDIA OF CHEMICAL REACTIONS. Compiled by C. A. JACOBSON. Edited by CLIFFORD A. HAMPEL. Volume VIII: Tungsten, Uranium, Vanadium, Ytterbium, Yttrium, Zinc, Zirconium and Addenda. Pp. x + 533. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1959. Price $14.00; 112s.

SELECTED METHODS OF ANALYSIS OF FOUNDRY MATERIALS. Part 1. PIG IRON AND CAST IRON. Pp. 97. Birmingham: The British Cast Iron Research Association. Price 17s. 6d.; $2.50.

TABLES OF PHYSICAL AND CHEMICAL CONSTANTS. Originally compiled by G. W. C. KAYE, O.B.E., M.A., D.Sc., F.R.S., and T. H. LABY, M.A., Sc.D., F.R.S. Now prepared under the Direction of an Editorial Committee. Twelfth Edition. Pp. viii + 231. London, New York and Toronto: Longmans, Green & Co. Ltd. 1959. Price 25s.

Erratum

JUNE (1959) ISSUE, p. 334. In the Programme of Work of the Prophylactics Panel, delete (pyrimethamine) after Nicarbazin.